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# A petrochemical study of Tertiary tholeiitic basalts: The Middle Lavas of the Antrim Plateau

E. M. Patterson
formerly Department of Geology, The University, St. Andrews*
and
D. J. Swaine
Department of Spectrochemistry,
The Macaulay Institute for Soil Research, Aberdeen

(*Received* 15 *June* 1955)

ABSTRACT
Nine basalts which occur as flows in the Middle Lava series of the Antrim Plateau have been analysed chemically and spectrographically. Seven of the specimens come from the complete flow succession in the neighbourhood of the Giant's Causeway. The petrochemistry of the major and trace elements is discussed.

## Introduction

The Tertiary lavas in the northern part of the Antrim Plateau have recently been separated into three sets of flows, designated respectively the Lower, Middle, and Upper Lava series (Patterson, 1955). Interbasaltic beds, chiefly of lateritic origin, divide the series from each other.

Within recent years a considerable amount of petrographic data for these lavas, including trace-element contents, has become available. In the present paper existing chemical data for the tholeiitic basalts of the Middle Lava series are amplified.

The spectrographic determinations of the trace elements have been carried out by one of us (D. J. S.) at The Macaulay Institute for Soil Research, Aberdeen, using the same techniques as for earlier analyses of lavas and intrusive rocks from north-east Ireland. We are indebted to the Director of The Macaulay Institute for permission to carry out this work. We also wish to thank J. Preston, The Geology Department, Queen's University, Belfast, for his assistance in collecting some additional material for spectrographic analysis.

## Geological Setting

Olivine-basalt flows constitute both the Lower and the Upper Lava series in the area. In contrast to these, the Middle series is made up of olivine-free or olivine-poor, tholeiitic basalt, occurring typically at the Giant's Causeway (Tomkeieff, 1940). Recent mapping of almost one hundred square miles of the Causeway hinterland has shown that the Middle Lavas form a wedge between the Lower and Upper series, which apparently thickens towards the north-east, beyond the present coastal limits (Patterson, 1955, pp. 89-95, 117).

* Present address : 25 Caldwell Road, West Kilbride, Ayrshire.

Immediately south-east of the town of Portrush two flows make up the Middle Lava series. In a traverse between the Causeway and the hamlet of Tonduff six flows can be mapped, while seven occur on Croaghmore, a hill south of White Park Bay. It is in this area that the flow sequence can best be studied and collected; further east the series is probably somewhat thicker, but individual flows cannot be traced far because of the lack of continuous exposures. Consequently, in the study of the Middle Lava series already made by one of us (E. M. P.), particular attention was paid to this type area, and the material for chemical analysis was selected from it.

## Petrochemistry of the Major Elements

In general, the tholeiitic basalts of north Antrim are petrographically similar to lavaform rocks belonging to the Hebridean Non-porphyritic Central Magma type, as defined by the Geological Survey (Bailey *et al.*, 1924). They correspond to Kennedy's definition of the Tholeiitic Magma type (1933) and to Tomkeieff's Causeway type (1949).

The majority of analyses of lavas of this rock type from the British Tertiary sub-Province have been made on material from Co. Antrim, where their areal distribution and stratigraphical position are known precisely. Analysed Mull lavas of this type are inevitably somewhat altered by their proximity to major intrusives and, as already pointed out, one of them must be regarded as atypical of the Non-porphyritic Central Magma type (Patterson, 1955, p.106; Guppy and Thomas, 1931, pp. 63–64, Analysis No. 241). The results from Antrim now give a more complete picture of the chemical characteristics than has previously been available from earlier work by Holmes (1936) and Patterson (1952).

In a recent petrochemical survey of the Antrim lavas, an attempt was made to calculate an average composition for each of the four rock types encountered (Patterson, 1952, p. 291). At that time only two chemically analysed tholeiitic basalts had also been analysed spectrographically for trace elements. The two spectrographic analyses were in reasonable agreement, and the average values for a number of elements were intermediate between those for olivine-basalts and quartz-trachyte. In view, however, of the fact that the average for tholeiitic basalt was based on only two results, it was clearly desirable to obtain further trace-element data for this rock type.

Table 1 contains the results of chemical analyses of those rocks for which spectrographic analyses are also available, recalculated to 100 per cent on a water and $CO_2$-free basis. This procedure has been followed so that satisfactory comparisons may be made between these rocks, and it is regarded as desirable when the major constituents in chemically similar rocks are being compared (Walker and Poldervaart, 1949, p. 648). The full chemical, normative, and modal analyses of these rocks have already been published (Patterson, 1955, Tables VIII–X). Analyses I to VII are of the colonnade or massive central portions of flows 1 to 7 respectively, selected from the mapped succession near to the Giant's Causeway. They form a complete section through the Middle Lava series and represent a series of lava-flows whose inter-relationship in time is clearly established.

*Table* 1. *Analyses of basalts of Middle Lava series*

Calculated water and $CO_2$-free to 100 per cent from data in *Proc. Roy. Irish Acad.*, **57**, B, Table VIII (1955), and *Geochim. et cosmochim. Acta*, **2**, 283–299 (1952).

| Analysis: | I | II | III | IV | V | VI | VII | VIII | IX | A |
|---|---|---|---|---|---|---|---|---|---|---|
| | % | % | % | % | % | % | % | % | % | % |
| $SiO_2$ | 51·6 | 52·0 | 51·9 | 51·6 | 51·6 | 52·6 | 54·9 | 54·8 | 48·0 | 47·2 |
| $Al_2O_3$ | 14·8 | 15·0 | 15·4 | 14·0 | 14·5 | 14·3 | 14·8 | 14·3 | 14·9 | 15·2 |
| $Fe_2O_3$ | 2·7 | 2·5 | 2·8 | 2·2 | 3·0 | 3·9 | 5·2 | 2·5 | 3·4 | 2·7 |
| FeO | 8·3 | 8·4 | 7·2 | 8·1 | 6·8 | 7·4 | 5·8 | 8·6 | 9·0 | 8·9 |
| MgO | 6·4 | 6·0 | 6·8 | 7·6 | 7·4 | 5·8 | 4·6 | 5·4 | 8·7 | 11·9 |
| CaO | 11·0 | 10·7 | 11·3 | 12·0 | 11·7 | 10·1 | 8·6 | 9·2 | 12·2 | 10·4 |
| $Na_2O$ | 2·5 | 2·7 | 3·0 | 2·7 | 3·1 | 3·0 | 2·4 | 2·6 | 2·4 | 2·0 |
| $K_2O$ | 1·0 | 0·9 | 0·4 | 0·5 | 0·4 | 0·8 | 1·5 | 1·1 | 0·1 | 0·2 |
| $TiO_2$ | 1·1 | 1·0 | 1·0 | 0·9 | 0·9 | 1·1 | 1·1 | 1·2 | 0·7 | 1·0 |
| $P_2O_5$ | 0·5 | 0·5 | tr. | 0·3 | 0·4 | 0·8 | 0·9 | 0·1 | 0·3 | 0·2 |
| MnO | 0·1 | 0·2 | 0·2 | 0·1 | 0·2 | 0·2 | 0·2 | 0·2 | 0·2 | 0·2 |
| $\frac{(FeO + Fe_2O_3) \times 100}{MgO + FeO + Fe_2O_3}$ | 63 | 65 | 60 | 58 | 57 | 66 | 71 | 67 | 59 | 47 |
| $\frac{K_2O \times 100}{K_2O + Na_2O}$ | 29 | 25 | 11 | 16 | 11 | 21 | 38 | 30 | 4 | 9 |
| $\frac{Fe_2O_3 \times 100}{FeO + Fe_2O_3}$ | 25 | 23 | 28 | 21 | 31 | 34 | 47 | 22 | 28 | 23 |

I—No. 1 flow. Grand Causeway, Aird townland.
II—No. 2 flow. Port na Spaniagh, Aird townland.
III—No. 3 flow. Scarp 100 yards south-east of Portnacallian Head, Lisserluss townland.
IV—No. 4 flow. Disused quarry quarter mile south of Plaiskin Farm, Tonduff Mountain townland.
V—No. 5 flow. Cliff west of Dunseverick Castle, Feigh townland.
VI—No. 6 flow. Small disused quarry, 100 yards north-east of hamlet, Tonduff townland.
VII—No. 7 flow. North-west of summit of Croaghmore hill, Croaghbeg townland.
VIII—No. 2 flow. Disused quarry, quarter mile north of Scudion Craig, Urbalreagh townland.
IX—No. 6 flow. Cliff, Portnabrock, quarter mile west-north-west of Portbraddan, Templastragh townland.
A—Average of six olivine-basalt lavas from Antrim Plateau.

The basalt from Scudion Craig, east-south-east of Portrush (Table 1, Analysis VIII) was taken between seven and ten miles south-west of the foregoing. Though nominally the second flow in the series, because of regional thinning it is also the final flow. Hence it is not necessarily contemporaneous with either the second flow at Port na Spaniagh or the final flow on Croaghmore (Table 1, Analyses II and VII), and its relative position in the extrusion time-scale is not known.

The basalt from Portnabrock (Table 1, Analysis IX) on the coast east of the Causeway is the most basic of the Middle series lavas, both on silica percentage and on the iron/magnesium ratio. It lies sixth in the flow succession, but from its field relations appears to be of restricted extent. The rock is distinctive in containing 6 per cent of modal olivine, a feature reflected in its chemistry, which differs from the rest of the analysed basalts from the Middle Lava series. It has a closely similar composition to the well-known basalt of Staffa (Patterson,

1955, Table XI, Analysis E), but differs in its exceptionally low potash content, which is only one-tenth that of the Hebridean rock. In its potash content and high Na/K ratio the Portnabrock lava differs from the majority of analysed British Tertiary basalts.

Consideration of the chemical characteristics of the flow sequence near to the Causeway (Table 1, Analyses I–VII) shows initially that the silica percentage is almost constant from the first to the sixth flows, averaging 51·9 per cent and having a mean variation of 0·3 per cent. Only the final flow is appreciably more siliceous than the others. It was clear that comparison of the contents of the remaining constituents on a silica/basic oxide diagram would yield no useful information.

The iron/magnesium ratio $\frac{(FeO + Fe_2O_3) \times 100}{MgO + FeO + Fe_2O_3}$ was first utilized by Wager and Deer (1939) to provide an index of the degree of crystal fractionation of basaltic magma in the Skaergaard instrusion, East Greenland. This ratio appears to yield, for the present closely related series of analyses, a more significant set of comparative values than does the silica percentage. The iron/magnesium ratios fall within fairly close limits, but show a definite fall in the middle flows of the series, while there is a small increase between the first and second flows which is probably without significance (Fig. 1a). It may be thought that such small variations in the ratios could be the result of analytical errors; against this, however, adequate confirmation of the validity of the chemically determined results is provided by the trends of certain trace elements.

Presumably the basalts of flows 1 to 7 are the products of successive expulsions of magma from a single source over a long period of time. The source magma has been affected by two contrasted processes during that period: one producing enrichment in iron relative to magnesium, the other producing the reverse effect. The first of these is exemplified by the trend of Fig. 1a between flows 1 and 2, and between 5 and 7, the second process in the reverse slope between flows 2 and 5.

Two other distinct chemical trends are apparent in the series. The degree of oxidation of iron $\frac{Fe_2O_3 \times 100}{FeO + Fe_2O_3}$ increases in the second half of the series. There is also a marked drop in the potash/soda ratio $\frac{K_2O \times 100}{K_2O + Na_2O}$. Potash indeed varies more widely in the Middle Lava series than does any other major element, the maximum of 1·5 per cent in flow 7 being almost four times as great as the minima in flows 3 and 5 (Fig. 1c). An "average" value for potash in these lavas, if they are all to be regarded as typically tholeiitic basalts, can have little absolute meaning.

The flow from Scudion Craig, on the western limits of the series (Analysis VIII), possesses chemical characteristics which are between those of the penultimate and final flows from the Causeway hinterland, a fact perhaps in keeping with its uppermost position in the attenuated succession where it occurs.

## Petrochemistry of the Trace Elements

With the exception of phosphorus and manganese, the trace elements were determined spectrographically by a similar semi-quantitative method to that described by Mitchell (1948). A mixture of equal weights of the finely ground

rock and carbon powder was filled into a carbon electrode which was used as cathode in a 9-ampere d.c. arc. Two one-minute exposures were taken on each of two plates, covering the ranges 2470–3550 Å and 3180–8000 Å, a Hilger Large Quartz Spectrograph (E492) being used. The spectrograms were compared visually against standard spectrograms in a Hilger Projection Spectrum Comparator. When the basic composition of the samples is similar to that of the standard, the precision is of the order of $\pm 30$ per cent. The nine samples were not done at the same time, but in three batches of one, two, and six, new standards being prepared on each occasion.

Table 2 gives the contents of the trace constituents expressed as parts per million of the element. In the following discussion, Analyses I to VII, coming from

*Table 2. Trace element contents*
*(as parts per million)*

| Analysis: | $r$ | $s$ | I | II | III | IV | V | VI | VII | VIII | IX | B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $P^{5+}$ | 0·34 | — | 1930 | 2150 | tr. | 1350 | 1500 | 3400 | 3800 | 600 | 1430 | 1700 |
| $Ga^{3+}$ | 0·62 | 1 | 40 | 25 | 15 | 15 | 20 | 20 | 25 | 30 | 20 | 20 |
| $Cr^{3+}$ | 0·64 | 1 | 200 | 40 | 80 | 150 | 200 | 30 | 30 | 100 | 500 | 30 |
| $V^{3+}$ | 0·65 | 1 | 700 | 300 | 500 | 500 | 400 | 400 | 500 | 800 | 400 | 200 |
| $Li^{1+}$ | 0·78 | 1 | 20 | 6 | 5 | 5 | 5 | 7 | 10 | 15 | 3 | 5 |
| $Ni^{2+}$ | 0·78 | 3 | 70 | 40 | 40 | 50 | 60 | 20 | 15 | 30 | 100 | 30 |
| $Co^{2+}$ | 0·82 | 3 | 70 | 40 | 40 | 40 | 40 | 30 | 20 | 150 | 50 | 25 |
| $Cu^{2+}$ | 0·83 | 5 | 300 | 80 | 60 | 150 | 200 | 50 | 25 | 60 | 200 | 300 |
| $Sc^{3+}$ | 0·83 | 10 | 20 | 25 | 30 | 20 | 30 | 30 | 20 | 30 | 20 | <10 |
| $Zr^{4+}$ | 0·87 | 10 | 700 | 150 | 100 | 60 | 80 | 80 | 200 | 700 | 60 | 100 |
| $Mn^{2+}$ | 0·91 | — | 920 | 1700 | 1800 | 850 | 1300 | 1700 | 1700 | 1800 | 1700 | 1850 |
| $Y^{3+}$ | 1·06 | 10 | 70 | 40 | 40 | 40 | 40 | 40 | 60 | 70 | 30 | <30 |
| $La^{3+}$ | 1·22 | 10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 | 10 | <10 | <30 |
| $Sr^{2+}$ | 1·27 | 3 | 500 | 400 | 500 | 500 | 300 | 500 | 500 | 2000 | 300 | 200 |
| $Pb^{2+}$ | 1·32 | 10 | 10? | <10 | <10 | <10 | <10 | <10 | <10 | 10? | <10 | <10 |
| $Ba^{2+}$ | 1·43 | 5 | 700 | 300 | 200 | 200 | 200 | 500 | 500 | 2000 | 20 | 40 |
| $Rb^{1+}$ | 1·49 | 1 | 30 | 10 | 2 | 1 | <1 | 5 | 40 | 150 | <1 | <20 |

$r$ = ionic radius in Ångstrom units (Goldschmidt, 1954).
$s$ = minimum sensitivity in parts per million.
The following elements are not present in an amount greater than $s$ (in brackets): Ag (1), As (3000), Be (5), Bi (30), Cd (200), Ge (10), Hg (1000), In (10), Mo (1), Sb (300), Sn (5), Tl (10), Zn (300).
Lines were not found for Au, Ir, Pt.
Localities for specimens I to IX correspond to those listed in Table 1.
B—Tholeiitic basalt, Blosseville Coast, East Greenland (Wager and Mitchell, 1951).
Analyst : D. J. Swaine (values for phosphorus and manganese determined chemically by E. M. Patterson).

flows 1 to 7, will often be considered together as a group. The Scudion Craig and Portnabrock basalts, already mentioned as coming outside the normal flow succession, will be referred to individually. Reference will be made to analyses of the constituents of the Kinkell tholeiite, Stirlingshire (Walker, Vincent, and Mitchell, 1952), and the data for a specimen of tholeiitic basalt from the Blosseville Coast, East Greenland (Wager and Mitchell, 1951) have been included in Table 2 for comparison with the Antrim figures.

*Phosphorus* shows fairly wide variations from flow to flow, but in general the amounts are normal for this section of the British Tertiary igneous rocks (Richey, 1937, p. 47 and Fig. 2). Only in flows 6 and 7 from the Causeway area (Analyses VI and VII, Table 2) do the amounts rise significantly above the mean, or above the value for the Blosseville Coast sample.

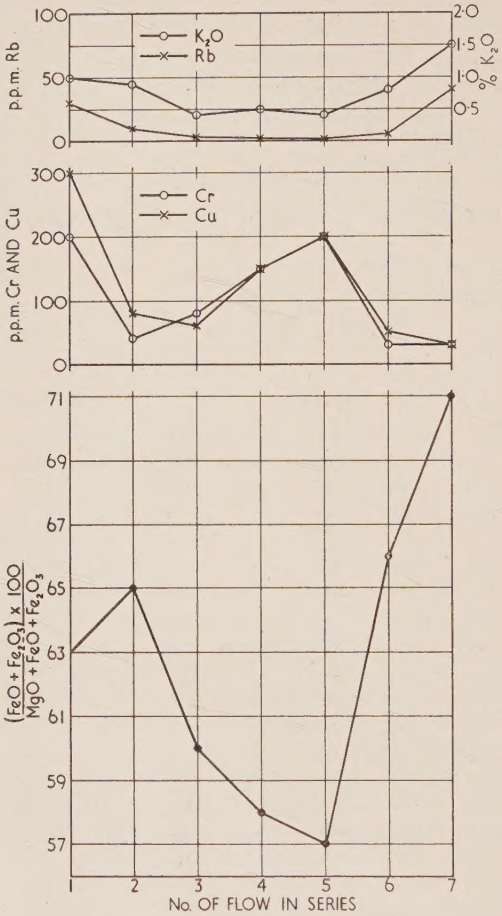


Fig. 1c. Variation of rubidium and potassium in Middle series lava flows.

Fig. 1b. Variation of chromium and copper in Middle series lava flows.

Fig. 1a. Variation of iron/magnesium ratio in Middle series lava flows.

*Gallium* is sensibly constant with a mean of about 20 p.p.m. This is not surprising, since there is an almost constant amount of aluminium in the rocks. The average gallium content now reported is somewhat less than the figure of 35 p.p.m. given in an earlier paper for these lavas (Patterson, 1952, p. 291).

*Chromium* varies in a rather unexpected way which is difficult to relate to the basicity of the different specimens. Maxima occur in flows 1 and 5 (see Fig. 1b). As would be expected from its mineralogy and from its chemical analysis, the Portnabrock olivine-bearing rock is higher in chromium than any of the other specimens from the Middle Lava series, though the amount of 500 p.p.m. is lower than in any of the six olivine-basalts from Antrim (Patterson, 1951, p. 290).

*Vanadium* maintains a fairly uniform abundance with a mean content of about 400 p.p.m., about twice that present in the Blosseville Coast rock. The previously calculated average of 750 p.p.m. for the Antrim tholeiitic basalt is apparently rather too high.

*Lithium.* The amounts of lithium in the middle flows of the series are more or less of the order to be expected in basic rocks. The values for flows 2 to 6 are remarkably constant (5–7 p.p.m.) and agree well with the 5 p.p.m. of the Blosseville Coast rock. In flows 1 and 7, and in

the Scudion Craig specimen, the amount of lithium is distinctly greater in keeping with the less basic character of these flows. The fourfold variation in the amount of lithium from 5 to 20 p.p.m. makes an average value for this element of little significance.

*Nickel* and *Cobalt*. As regards these two elements, there is a tendency for lower values in flows 6 and 7, which is in keeping with the slightly lower magnesium values. The higher cobalt in the Scudion Craig flow is associated with a higher ferrous iron, but a similar increase in cobalt does not occur in the Portnabrock basalt. The comparative abundance of nickel in the latter is associated with an increase in magnesium, shown by the appearance of olivine.

In flows 1 to 7 the ratio of nickel to cobalt is fairly close to 1 : 1, but in the Scudion Craig and Portnabrock samples this ratio is 1 : 5 and 2 : 1 respectively. The significance of this ratio has been commented upon by LUNDEGÅRDH (1946) and by WAGER and MITCHELL (1951, p. 189), and the results obtained for the Antrim rocks are in accordance with their varying iron/magnesium ratios.

*Copper*. Its variations are remarkably akin to those displayed by chromium (see Fig. 1b), and commented on above. In view of the considerable variations in the amount present, the calculation of an average is perhaps scarcely admissible, but the figure obtained (125 p.p.m.) appears to be about average for basic rocks (WAGER and MITCHELL, 1951, p. 190).

*Scandium*. The amounts of this element in all the rocks analysed are remarkably constant, the mean value being around 25 p.p.m. It is not surprising to find scandium, since its ion is able to replace magnesium or ferrous iron in the pyroxene. It is noteworthy that scandium appears to be considerably more abundant than in many of the Skaergaard rocks, while it was not detected in the tholeiitic basalt from the Blosseville Coast, i.e., it is below 10 p.p.m. in that rock.

*Zirconium*. Corresponding to increasing basicity, as shown by the iron/magnesium ratio, there is a well-marked decrease in the amount of zirconium in the middle flows of the series, followed by a rise in the seventh flow. Zirconium is similarly abundant in the Scudion Craig specimen. An average value has obviously little meaning when the range of values is from 60 to 700 p.p.m., and the figure quoted previously for the Antrim tholeiitic basalts is now seen to be at the upper limit for this group of rocks. The 100 p.p.m. found in the Blosseville Coast rock is of the same order as the values found for flows 2 to 6, and is within the range for the Middle Lava series as a whole.

*Manganese*, determined colorimetrically using the periodate oxidation method, varies but little throughout the series of specimens. The amount of this element present is of the same order as in the Antrim olivine-basalts, the Skaergaard parent magma and the olivine and tholeiitic basalts of the Blosseville Coast.

*Yttrium* is fairly constant at about 40 p.p.m., a figure which is above that of the Blosseville Coast olivine and tholeiitic basalts, in which the element was never present above the limit of sensitivity of 30 p.p.m. The average calculated for the nine analysed samples is somewhat less than that given for the two tholeiitic basalts in an earlier paper (PATTERSON, 1952, p. 291), but nevertheless appears to confirm that relative abundance in yttrium is characteristic of the basic lavas in north-east Ireland.

*Lanthanum* failed to rise above the limit of sensitivity in all of the rocks analysed, and it is not therefore possible to say whether or not this trace element resembles yttrium in being relatively abundant in the Antrim basalts.

*Strontium*. The mean value, excluding the Scudion Craig rock, is around 400 p.p.m., and is twice the mean value for basalts calculated from NOLL's data (GOLDSCHMIDT, 1954). The much higher content of 2000 p.p.m. in the Scudion Craig basalt can perhaps be attributed to the glassy mesostasis; it is interesting to note that barium and rubidium are also high in this rock, and it was shown in the examination of the Kinkell tholeiite that strontium, barium, and rubidium are concentrated in the glass. This high content in the Scudion Craig rock caused the earlier overestimation of strontium in the Antrim tholeiitic basalts (PATTERSON, 1952, p. 291), the figure quoted therein being three times as great as the average in flows 1 to 7.

*Lead*. With the limit of sensitivity for lead reduced to 10 p.p.m., it now appears that the amount of this element in the tholeiitic basalts averages less than 10 p.p.m., and the figure of 25 p.p.m. given tentatively for this rock type (PATTERSON, 1952, p. 296) is much too high. The present amount falls into line with that occurring in the Blosseville Coast basalts and basic

rocks from many other areas. Lead was not detected in the plagioclase, augite, iron ore, or glass separated from the Kinkell tholeiite.

*Barium.* The variation in the amount of barium in flows 1 to 7 reflects the trend of potassium. The mean value of about 300 p.p.m. is considerably higher than the 40 p.p.m. of the Blosseville Coast basalt, a fact probably accounted for by the higher content of potassium in the Antrim samples. The relative abundance of barium and strontium in the Antrim basalts in general has been commented upon already (Patterson, 1952, p. 297). As would be expected, the basic rock from Portnabrock, which is remarkably low in potassium, has only 20 p.p.m. of barium, an amount more in keeping with the Greenland rocks.

*Rubidium* shows a very marked decrease from flow 1 to flow 5 and then increases to flow 7. This striking variation follows the behaviour of potassium (see Fig. 1c), and, as would be expected, is more pronounced than the latter element. The most potassium-rich of the tholeiitic basalts (Analysis VII) contains over forty times as much rubidium as those low in potassium, while an even higher content is shown by the Scudion Craig rock. It is interesting to note that the rocks which are lowest in rubidium (Analyses III, IV, V) contain less of this element than some of the olivine basalts of the Antrim Plateau. It is apparent that in the Middle Lava series of Antrim both the actual amount of rubidium and also the rubidium/potassium ratio increase rapidly with decrease in basicity. There is such a wide variation in the rubidium content that calculation of an average value is inadmissible. Both the values used in the calculation of an average previously are now seen to be among the higher values obtained in the present, more detailed study.

## Summary and Conclusions

Chemical and spectrographic analyses have been made of basalts which occur as flows in the Middle Lava series of the Antrim Plateau. These flows display a general uniformity in their petrography, and their field relationships indicate that they had been erupted over a long period of time.

Chemically the Middle series flows show a decided kinship, but certain well-marked variation trends can be distinguished. So far as the major elements are concerned, these variations are seen as:

1. Increase in basicity (measured by the iron/magnesium ratio) in the middle flows of the series.

2. A concomitant fall in the absolute content of potassium and in the potassium/sodium ratio.

The significance of these results, which occur within close limits of silica content, is fully confirmed by the behaviour of certain trace elements. Rubidium in particular follows in expected fashion the potassium trend, and falls to below one-fiftieth in the middle, potassium-poor, flows, compared with earlier and later flows. Barium shows the same trend, to a lesser degree.

The average granularity of these basalts varies from 0·03 to 0·05 mm, and this extreme fineness of grain unfortunately makes an efficient separation of the different mineral fractions a practical impossibility. In the absence of chemical data for the minerals, the distribution of the trace elements in the minerals of the rocks remains unknown, and speculation regarding the possible causes of the variations is scarcely justified.

It appears that at the level or levels at which the magma chamber was being tapped during the extrusion of these flows there was a definite variation in the chemical characteristics with the passage of time. Unexpectedly large variations in the contents of certain trace elements are associated with smaller observed changes in the major elements, such as the iron/magnesium ratio. The addition

of early-formed olivines from higher levels in the magma chamber, while perhaps competent to account for the increasing basicity of the middle flows, is not reflected by the behaviour of nickel, and fails to account for the unexpectedly large variations in the alkali metals.

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# The origin of some New Zealand metamorphic rocks as shown by their major and trace element composition

S. R. Taylor*
Department of Geology, Indiana University

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ABSTRACT

In a study of a portion of the regionally metamorphosed Alpine Schist Belt, South Island, New Zealand, where thin beds of green schists are interbedded with quartz-albite-biotite schists,the redistribution of the chemical elements by metamorphism is shown to have been slight, so that chemical data can be used to indicate the nature of the parent rock.

Ten analyses are reported for the quartz-albite-biotite-(calcite)-(clinozoisite) schists (Arahura series). The distribution of the elements, in particular, P, V, Mn, Na, Ca, Sr, K, and Ba, indicates that the parent rocks were of greywacke type composed of essentially unweathered minerals, while the source rocks were high in alkali feldspar.

Seven analyses are given for the green schists (Pounamu Series). They show significantly higher amounts of Cr, Mg, Ni, Co, and Cu and lower amounts of P, Ti, Sr, Ba, and K compared with the enclosing Arahura schists. One group of three ten-foot beds is interpreted as being derived from sills of basaltic composition. A thicker unit is of more basic (olivine or picrite basalt) composition, and the distribution of Cr, Fe, Mg, Ti, Ni, Co, Cu, V, Sc, Na, and Ca indicates gravitational differentiation in the original sill. It is also concluded that the intrusion took place prior to deformation as well as metamorphism.

## Introduction

Geochemical studies on metamorphic rocks have not been common, and there is little agreement or indeed evidence on the effect of metamorphic processes on the distribution of elements. While metasomatism by definition involves migration of elements over considerable distances, doubt exists on the amount and scale of chemical redistribution brought about by metamorphism with no introduction of material (Turner, F. J., in Ahrens, 1954, p. 815). If, for example, regional metamorphism, without notable introduction of chemical elements from external sources, causes elements to migrate over distances of only a few centimetres, we can, by taking adequate sampling precautions, deduce the nature of the parent rock from chemical analyses. On the other hand, the possibility arises that chemical gradients may be set up leading to transfer and exchange of material over much greater distances, so that primary variations due to igneous or sedimentary processes are obliterated and replaced by a distribution pattern depending

* Now at Department of Geology and Mineralogy, Oxford.

entirely on metamorphic effects. In this case it would be difficult to deduce the nature of the original rock by chemical means.

The area studied forms a small portion of a regionally metamorphosed terrain, the Alpine schist belt of the South Island, New Zealand, where narrow bands of green schists occur in many places, interbedded with schists of sedimentary origin. A petrological and chemical study of a typical sequence was undertaken, partly because these rocks have been little studied, and also to test the above ideas on the application of chemical data to the solution of metamorphic problems. The results of the petrological investigations have been reported elsewhere (Mason and Taylor, 1955).

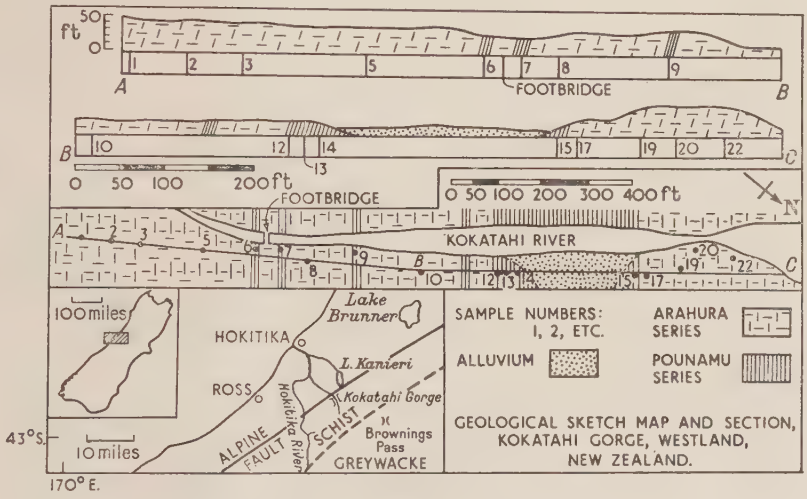


Fig. 1.

The lower gorge of the Kokatahi River, which provides a clear and accessible section through several narrow bands of green schists interbedded with quartz-albite-biotite schists, was selected for study. Bell and Frazer (1906) referred to the green schists of the Hokitika district, Westland, as the "Pounamu series," and to the widespread quartz-albite-biotite schists as the "Arahura series," and these names have been generally adopted for similar rocks in adjacent areas and are so used in this paper. Fig. 1 gives a geological sketch map and section with the location of the samples. The area is covered by sheet S.58 (unpublished) of the Lands and Survey Department Provisional One-Mile Series, and by a geological map of the Toaroha Survey District (Morgan, 1908). The mineralogical composition of the samples is summarized in Tables 1 and 3.

The Arahura and Pounamu rocks belong to the biotite zone (for regional metamorphism of greywacke) and, in the more general classification, are placed in the albite-epidote-amphibolite facies. The field relations and petrology as discussed in the previous paper give no evidence of post-metamorphic intrusion of the green schists. The age of these rocks is not certain, but they may not be much older than Triassic, for they grade eastward through chlorite-zone rocks into greywackes of Triassic age, and Wellman (1952, p. 17) notes that "except

*Table* 1. *Mineral composition, Arahura series*

| | *Quartz* | *Albite* | *Biotite* | *Muscovite* | *Chlorite* | *Tourmaline* | *Epidote* | *Clinozoisite* | *Garnet* | *Magnetite* | *Sphene* | *Opaque* | *Calcite* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T-1 | 16 | 25 | 45 | 3 | 1 | — | — | 8 | — | — | 2 | — | — |
| T-2 | 15 | 25 | 40 | 9 | — | — | — | 7 | 2 | — | 2 | — | — |
| T-3 | 25 | 25 | 30 | 13 | — | — | — | 5 | — | — | 2 | — | — |
| T-5 | 30 | 30 | 15 | 10 | — | 5 | — | 5 | 1 | 2 | 2 | — | — |
| T-8 | 20 | 45 | 10 | 1 | 3 | 3 | — | 10 | 6 | 2 | — | — | — |
| T-10 | 30 | 25 | 10 | 10 | 3 | — | — | 7 | — | — | — | — | 15 |
| T-17 | 1 | 6 | 5 | — | 1 | — | 1 | — | — | — | — | 2 | 85 |
| T-19 | 30 | 27 | 15 | 15 | 4 | 1 | — | 5 | 2 | — | — | 2 | — |
| T-20 | 30 | 27 | 15 | 15 | 4 | 1 | — | 5 | 2 | — | — | 2 | — |
| T-22 | 20 | 20 | 1 | — | 5 | — | 10 | 15 | — | — | — | 5 | 40 |

*Table* 2. *Major constituents expressed as oxides, Arahura series—Analyst*: S. R. Taylor

| | $P_2O_5$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$[1] | MgO | $TiO_2$ | $Na_2O$ | CaO | $K_2O$ | $CaCO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| T-1 | 0·23 | 61·2 | 14·4 | 9·31 | 4·89 | 1·05 | 2·60 | 1·77 | 4·07 | — |
| T-2 | 0·22 | 67·0 | 14·6 | 5·25 | 1·96 | 0·83 | 3·57 | 3·20 | 2·81 | — |
| T-3 | 0·39 | 59·7 | 13·0 | 8·29 | 1·59 | 1·30 | 7·41 | 2·45 | 5·40 | — |
| T-5 | 0·16 | 71·2 | 14·3 | 4·07 | 1·56 | 0·55 | 2·94 | 1·88 | 2·87 | — |
| T-8 | 0·21 | 52·5 | 28·9 | 5·08 | 3·07 | 0·67 | 5·05 | 3·20 | 0·88 | — |
| T-10 | 0·21 | 71·2 | 10·0 | 3·89 | 1·39 | 0·37 | 1·77 | — | 2·11 | 8·8 |
| T-17 | 0·13 | 15·3 | 5·60 | 3·56 | 2·57 | 0·15 | 1·15 | — | 0·23 | 70·9 |
| T-19 | 0·18 | 53·3 | 29·8 | 5·28 | 2·29 | 0·68 | 2·78 | 1·66 | 3·49 | — |
| T-20 | 0·23 | 53·7 | 29·0 | 5·95 | 2·57 | 0·72 | 1·89 | 1·75 | 3·73 | — |
| T-22 | 0·23 | 46·9 | 11·7 | 11·8 | 4·14 | 0·92 | 2·16 | — | 0·24 | 21·7 |

[1] Total iron expressed as $Fe_2O_3$.

*Table* 3. *Mineral composition of green schists* (*Pounamu series*)

| | *Quartz* | *Albite* | *Biotite* | *Chlorite* | *Hornblende* | *Epidote* | *Clinozoisite* | *Rutile* | *Opaque* | *Calcite* |
|---|---|---|---|---|---|---|---|---|---|---|
| T-6 | 20 | 20 | 5 | 10 | 30 | 8 | — | 2 | — | 5 |
| T-7 | 25 | 22 | 2 | 30 | — | — | 15 | 1 | — | 5 |
| T-9 | 25 | 30 | 10 | 1 | 20 | — | 10 | — | 5 | — |
| T-12 | — | — | 20 | 10 | 60 | 10 | — | — | — | — |
| T-13 | 10 | 10 | 25 | — | 40 | 10 | — | — | — | 5 |
| T-14 | 25 | 25 | 1 | 20 | 3 | 6 | — | — | — | 20 |
| T-15 | 20 | 10 | 7 | 15 | 1 | 7 | — | — | — | 40 |

*Table* 4. *Major elements expressed as oxides, Pounamu series. Analyst*: S. R. TAYLOR

| | $P_2O_5$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$[1] | MgO | $TiO_2$ | $Na_2O$ | CaO | $K_2O$ | $CaCo_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| T-6 | 0·46 | 54·8 | 11·2 | 10·1 | 6·96 | 0·65 | 2·30 | 7·0 | 0·42 | 5 |
| T-7 | 0·10 | 53·5 | 14·2 | 7·45 | 9·28 | 0·65 | 6·54 | 2·4 | 0·51 | 5 |
| T-9 | 0·14 | 52·8 | 18·5 | 9·26 | 5·06 | 1·18 | 1·68 | 9·61 | 1·37 | — |
| T-12 | 0·13 | 51·1 | 12·3 | 11·2 | 14·3 | 0·22 | 0·74 | 8·92 | 0·89 | — |
| T-13[2] | 0·050 | 56·5 | 9·60 | 9·59 | 10·3 | 0·046 | 0·96 | 7·3 | 0·27 | 5 |
| T-14 | 0·037 | 53·0 | 11·6 | 6·48 | 7·88 | 0·043 | 1·50 | — | 0·20 | 18·9 |
| T-15 | 0·062 | 43·0 | 8·61 | 6·82 | 8·79 | 0·033 | 0·42 | — | 0·24 | 32 |

[1] Total iron expressed as $Fe_2O_3$.
[2] Average of 4 samples.

for the gradual decrease in metamorphism, there is no abrupt change in lithology from the schists into these fossiliferous sediments, and no reason for suspecting an unconformity." Metamorphism presumably took place during the post-Hokonui orogeny in the Lower Cretaceous.

The analytical data are presented in Tables 2 and 5 for the quartz-albite-biotite (Arahura) schists, and in Tables 4 and 6 for the green schists (Pounamu series). In Tables 2 and 4 the analyses of the "major elements" are expressed as oxides to facilitate comparisons with published analyses, while in Tables 5 and 6 they are given as the elements in order of increasing ionic radius. The ionic radii are from AHRENS (1952). The analytical methods used, a combination of colorimetric, flame photometric, and spectrographic techniques, have been described elsewhere (LEININGER and TAYLOR, 1954). Iron, titanium, and phosphorus were determined colorimetically, sodium and potassium by flame photometer, and the remaining elements by spectrographic procedures.

Rock samples were crushed between cellulose acetate sheets in an F. S. Carver press to minus 20-mesh and ground to minus 100-mesh in an agate mortar. Plastic sieve holders and bolting cloth were used. One gram of sample was warmed overnight with 10 ml $H_2SO_4$ and 20 ml HF in a 400 ml platinum dish with cover. After slow evaporation to 5 ml, 100 ml of water was added; after heating, the contents of the dish were filtered on Whatman No. 40 paper. The pH was adjusted to 1·3–1·8 by dissolving the precipitate formed upon addition of conc. $NH_4OH$ with conc. $H_2SO_4$; four drops excess acid are added. This solution was diluted to 250 ml.

Iron, titanium, and phosphorus were determined, using a Beckman DU Spectrophotometer with 25-mm diameter tubes and a blue sensitive photomultiplier tube. Iron was determined by measuring the absorbance at 380 mu of the $FeCl_3$ formed by mixing one volume of 1 : 9 dilution of the sample solutions with four volumes of 1 : 1 HCl. Titanium was determined by measuring the absorbance at 400 mu of titanium peroxide formed by mixing equal volumes of sample solution and reagent (1, 1 : 1 $H_2SO_4$; 1, $H_3PO_4$; 1, 30 per cent $H_2O_2$; 7, $H_2O$). Phosphorus was determined by measuring the absorbance at 430 mu of the molybdivanado-phosphoric acid complex formed by mixing five volumes of sample solution and two volumes of reagent (1·25 g ammonium metavanadate in 400 ml 1 : 1 $HNO_3$ mixed with 50 g ammonium molybdate in 600 ml $H_2O$). Sodium and potassium were determined with the Beckman DU Spectrophotometer with flame-photometer attachment. 1 : 9 dilutions of the sample solution were atomized into an oxygen-acetylene flame. Sodium was determined at 589 mu (blue-sensitive photomultiplier tube); potassium was determined at 767 mu (red-sensitive phototube). Subtractions for background were found superior to blank corrections. For the procedures outlined, the ranges in percent are: Fe, 0·35–25; Ti, 0·005–2·5; P, 0·003–5·0; Na and K, 0·1–10. Bureau of Standards samples and

G-1 and W-1 were used in calibration. Two spectrographic methods were employed. The first method using a $SrCO_3$ matrix gave values for Be, B, Ca, Co, Cr, Cu, Ge, Pb, Mg, Mn, Mo, Ni, Sc, Sn, Y, Zr, and $Al_2O_3/SiO_2$. $Al_2O_3$ and $SiO_2$ were determined from the intensity ratio Al/Si by the mutual standard method of calculation. A Jarrell-Ash 21-foot grating spectrograph was used with E.S.A.2 film in the wavelength range 2300–3550 Å. A mixture of one part each of sample and $SrCO_3$ and four parts of National SP-2 graphite was arced at 7 amp d.c. (adjusted arc-gap of 3·3 mm) for 120 sec. The anode sample cup was cut from National Spectrographic Special Graphite $\frac{1}{4}$-inch diameter to form a cup $\frac{1}{16}$-inch diameter, $\frac{1}{4}$-inch deep, with minimum wall thickness. The cathode was $\frac{1}{16}$-inch diameter Special Graphite. Intensity was controlled by a rotating sector. Strontium was the internal standard.

A second method allowed the determination of Ba, Co, Cr, Ga, La, Mn, Ni, Sc, Sr, and V. A mixture was made of two parts sample, one part SP-2 graphite and one part of a ferric oxide-palladium mixture which was varied to ensure 5 per cent Fe in all final mixtures. This final mixture was arced at 10-amp d.c. (adjusted arc-gap of 3·3 mm) for 90 sec. The anode sample cup was cut from National Spectrographic Special Graphite $\frac{3}{16}$-inch diameter to form a cup $\frac{1}{16}$-inch diameter, $\frac{1}{4}$-inch deep, with minimum wall thickness. The cathode was $\frac{1}{16}$-inch diameter Special Graphite. Eastman 103-0 film was used; the wavelength range was 3400–4650 Å. Intensity was controlled by a rotating sector. Iron was the internal standard. G-1, W-1, Bureau of Standards samples and synthetic standards were used to construct working curves.

## The Distribution of the Elements in the Quartz-albite-biotite Schists (Arahura series)

The Alpine schist belt, of which these rocks form a part, is the north-eastward extension of the widespread Otago schists. These broad areas of mainly low-grade metamorphic rocks show much petrological and field evidence of derivation from greywacke and associated sedimentary types. Hence, in the following discussion, the analytical figures for the quartz-albite-biotite (Arahura series) schists are compared with the average greywacke composition given by Pettijohn (1949, p. 250, anal. G); with two analyses of New Zealand greywacke quoted by Turner (1948, p. 117); with various averages from Rankama and Sahama (1950); and with the figures reported for the pelitic Littleton formation, New Hampshire, of Devonian age, by Shaw (1954).

Boron is present in the four rocks (T-5, T-8, T-19, and T-20) which contain tourmaline. The presence of tourmaline has been held to indicate boron and sodium metasomatism from subjacent granite intrusives. This explanation for the widespread occurrence of tourmaline in the Otago schists was adopted by Hutton (1940, pp. 63-65, 67, and 73). Rankama and Sahama (1950, p. 491) report an average abundance in shales of 310 p.p.m. boron, and it is thus conceivable that the boron required came from the original "clay" matrix of the greywacke.

Phosphorus ranges from 570 to 1700 p.p.m. (Turner, 1948, p. 117, 870 and 1180 p.p.m.; Pettijohn, 1949, p. 250, 440 p.p.m.). The amount of phosphorus contrasts with the averages reported by Rankama and Sahama (1950, p. 126, 1180 p.p.m. for igneous rocks, 350 p.p.m. for sandstones, 740 p.p.m. for shales, and 175 p.p.m. for limestones). The phosphorus content in the Arahura rocks indicates derivation from unweathered igneous minerals (apatite, garnet, etc.). During metamorphism, $P^{5+}$ (0·35 Å) probably substitutes for $Si^{4+}$ (0·42 Å) (Mason and Berggren, 1941.)

Silicon in the non-calcareous rocks ranges from 24·5 per cent (52·5 per cent

$SiO_2$) to 33·3 per cent (71·2 per cent $SiO_2$), reflecting varying amounts of quartz, feldspar, and "clay." (PETTIJOHN, 1949, p. 250, 30 per cent = 64·2 per cent $SiO_2$.)

*Table 5. Analyses of the quartz-albite-biotite schists (Arahura series) (expressed as parts per million)*

| | T-1 | T-2 | T-3 | T-5 | T-8 | T-10 | T-17 | T-19 | T-20 | T-22 |
|---|---|---|---|---|---|---|---|---|---|---|
| $B^{3+}$ | — | — | — | 68 | 430 | — | — | 36 | 49 | — |
| $P^{5+}$ | 1000 | 960 | 1700 | 690 | 910 | 920 | 570 | 800 | 1000 | 990 |
| $Si^{4+}(\times 10^3)$ | 28·6 | 31·3 | 27·9 | 33·3 | 24·5 | 33·3 | 7·17 | 24·9 | 25·1 | 21·9 |
| $Al^{3+}$ | 76100 | 77300 | 68800 | 75400 | 153000 | 52800 | 29600 | 158000 | 153000 | 62000 |
| $Cr^{3+}$ | 150 | 25 | 40 | 20 | 37 | 10 | 10 | 42 | 35 | 46 |
| $Fe^{3+}$ | 65100 | 36700 | 58000 | 28500 | 35500 | 27200 | 24900 | 36900 | 41600 | 82300 |
| $Mg^{2+}$ | 29500 | 11800 | 9600 | 9400 | 18500 | 8400 | 15500 | 13800 | 15500 | 25000 |
| $Ti^{4+}$ | 6300 | 5000 | 7800 | 3300 | 4000 | 2200 | 910 | 4100 | 4300 | 5500 |
| $Ni^{2+}$ | 82 | — | — | — | — | 32 | 47 | 64 | 61 | 100 |
| $Co^{2+}$ | 40 | — | — | — | 22 | 24 | — | 19 | 18 | 41 |
| $Cu^{2+}$ | 14 | 31 | 15 | 17 | 58 | 55 | — | 57 | 40 | 19 |
| $V^{3+}$ | 180 | 98 | 100 | 68 | 120 | 56 | 53 | 110 | 110 | 30 |
| $Zr^{4+}$ | 170 | 150 | 250 | 170 | 150 | 100 | — | 120 | 130 | <30 |
| $Mn^{2+}$ | 1150 | 800 | 580 | 520 | 5400 | 910 | 5100 | 800 | 820 | 3600 |
| $Sc^{3+}$ | 33 | — | — | — | — | — | — | — | — | 60 |
| $Y^{3+}$ | — | <20 | — | — | — | <20 | <20 | — | — | <20 |
| $Na^{+}$ | 19300 | 26500 | 55000 | 21800 | 37500 | 13100 | 8500 | 20600 | 14000 | 16000 |
| $Ca^{2+}$ | 12700 | 23000 | 17600 | 13500 | 23000 | 35400 | 284000 | 11900 | 12600 | 37000 |
| $Sr^{2+}$ | 195 | 125 | 380 | 300 | 100 | 280 | 165 | 125 | 225 | 115 |
| $Pb^{2+}$ | — | — | — | — | <50 | <50 | <50 | <50 | <50 | <50 |
| $K^{+}$ | 33800 | 23300 | 44800 | 23800 | 7300 | 17500 | 1900 | 29000 | 31000 | 2000 |
| $Ba^{2+}$ | 700 | 490 | 570 | 480 | 450 | 530 | 40 | 770 | 1500 | 70 |

The following elements were not present above the minimum detectability (in brackets): Ge (25), Be (100), Sn (50), Mo (50), La (100). — : not detected. T-10, T-17, and T-22 contain calcite. Analyst: S. R. TAYLOR.

Aluminium in the same rocks varies from 6·8 to 15·8 per cent, and is highest in those with lower silicon content, indicating a greater "clay" content (PETTIJOHN, 1949, p. 250, 7·4 per cent).

Chromium is present in rather uniform amounts (10 to 46 p.p.m.) except for T-1, where it reaches 150 p.p.m. (SHAW, 1954, 110 p.p.m.; RANKAMA and SAHAMA, 1950, p. 623, quartzites, 69-200 p.p.m., shales up to 600 p.p.m.). The high chromium content of T-1 is undoubtedly associated with the high biotite content. There is a general correlation between iron, magnesium, and chromium, and $Cr^{3+}$ (0·63 Å) is probably substituting for $Mg^{2+}$ (0·66 Å) and $Fe^{3+}$ (0·64 Å). Greywackes will contain chromium in the unweathered ferromagnesian minerals as well as that present in the resistant oxides.

The most important iron-bearing mineral is biotite, although chlorite and magnetite are occasionally present. Apart from the calcareous rocks, iron ranges from 2·9 to 6·5 per cent. (TURNER, 1948, p. 117, 3·0 per cent; PETTIJOHN, 1949, p. 250, 4·2 per cent.)

Magnesium is not present to any extent in the calcareous rocks, and this conforms with the absence of dolomite. In the whole series, it ranges from 0·84 to 3·0 per cent (Pettijohn, 1949, p. 250, 1·7 per cent), and is presumably contained in the biotite and chlorite.

Titanium is present in sufficient amount to form the separate mineral-phase sphene ($CaTiSiO_5$), and was presumably present as ilmenite or rutile in the original rock. The titanium content of the non-calcareous members of the Arahura series ranges from 3300 to 7800 p.p.m. (Pettijohn, 1949, p. 250, 3000 p.p.m.).

Nickel was not detected (<10 p.p.m.) in four rocks, but in the remainder it varies from 32 to 100 p.p.m. (Shaw, 1954, 64 p.p.m.). It is probably substituting for magnesium in chlorite, for this is the only mineral whose amount is parallel to the abundance of nickel. Cobalt shows a similar distribution, and where detected at >10 p.p.m. ranges from 18 to 41 p.p.m. (Shaw, 1954, 18 p.p.m.). It is presumably present in the chlorite. The abundance of nickel and cobalt in sediments is not well known; Rankama and Sahama (1950, p. 685) report 1 p.p.m. Co and up to 8 p.p.m. Ni in sandstones, although Goldschmidt (1954, p. 675) reports up to 50 p.p.m. In such rocks they are derived from magnetite and chromite grains, and may show much local variation. Rankama and Sahama (*loc. cit.*) quote 60 p.p.m. Co and 150 p.p.m. Ni in shales, and 8 and 24 p.p.m. respectively in aluminium-rich schists.

Copper ranges from 14 to 58 p.p.m. (Shaw, 1954, 18 p.p.m.; Rankama and Sahama, 1950, p. 700, shales 192 p.p.m.). No data are available for the abundance of copper in sandstones. The ease with which the copper minerals of igneous rocks are oxidized indicates that little of the element is to be expected in sandstones, and the copper content of the Arahura rocks is an indicator of the clay-mineral content of the original sediment.

Vanadium varies from 30 to 180 p.p.m. (Shaw, 1954, 120 p.p.m.; Rankama and Sahama, 1950, p. 601, sandstones 20 p.p.m., shales 120 p.p.m.). While, during weathering, vanadium will be largely removed, under the conditions of greywacke formation it may be expected to remain in the detrital ferromagnesian minerals.

Zirconium, not detected (<30 p.p.m.) in the highly calcareous sample (T-17), appears at 30 p.p.m. in the calcareous schist (T-22), but elsewhere ranges from 100 to 250 p.p.m. (Shaw, 1954, 200 p.p.m.; Rankama and Sahama, 1950, p. 567; shales 120 p.p.m., no figure for sandstones). The general resistance of zircon to weathering and the enrichment of zirconium in acidic igneous rocks indicates that it should closely accompany the quartz and feldspar.

Manganese, ranging from 910 p.p.m. to 5400 p.p.m., is closer to the Mn content of igneous rocks than to the average of 620 p.p.m. for shales (Rankama and Sahama, 1950, p. 652). In common with other elements such as copper and vanadium, the manganese content of the Arahura rocks indicates a large supply of incompletely weathered material.

Scandium was detected in only two rocks. $Sc^{3+}$ (0·81 Å) is closest in radius to $Fe^{2+}$ (0·74 Å), and presumably accompanies this element; for these rocks (T-1 and T-22) contain most iron.

Yttrium was detected in the calcareous rocks at <20 p.p.m. (Shaw, 1954,

45 p.p.m.). $Y^{3+}$ (0·92 Å) is common in limestone, diadochically replacing $Ca^{2+}$ (0·99 Å) (Rankama and Sahama, 1950, p. 528).

Apart from the calcareous rocks, sodium ranges from 1·4 to 5·5 per cent (Turner, 1948, p. 117, 2·9 per cent; Pettijohn, 1949, p. 250, 2·5 per cent). The high sodium content is noteworthy. It is the result of incomplete weathering, and sodium is chiefly present in detrital feldspar (Pettijohn, 1949, p. 250). During metamorphism, sodium forms albite, which is characteristic of schists derived from greywackes. While sodium metasomatism has been invoked to explain the presence of albite in similar rocks, Turner (1948, p. 116) states that greywackes and related rocks "contain sufficient soda to necessitate the occurrence of albite among the essential constituents of their low-grade metamorphic derivatives."

In the non-calcareous rocks, calcium ranges from 1·9 to 2·3 per cent (Pettijohn, 1949, p. 250, 2·5 per cent). The element must be derived, along with the sodium, from the detrital feldspar.

Strontium was detected in all rocks, ranging from 100 to 380 p.p.m. (Shaw, 1954, 710 p.p.m.). In the Arahura rocks the element shows no correlation with the amount of calcite, and its abundance is more characteristic of shales (average 170 p.p.m.) than limestones (average 425–765 p.p.m., Rankama and Sahama, 1950, p. 482). Strontium trends to form a separate phase (e.g. celestite, strontianite) in the sedimentary cycle, rather than replace calcium in calcite. It is thus likely that the strontium in the Arahura rocks, including the calcareous members, was derived from plagioclase feldspar and not from precipitation from sea-water, which is in accord with the environment of deposition.

Lead was detected in some of the Arahura rocks in amounts less than 50 p.p.m. (Shaw, 1954, 24 p.p.m.; Rankama and Sahama, 1950, p. 736, sandstones and shales 20 p.p.m.).

In the calcareous rocks, potassium is present at the low concentrations typical of limestones. Pettijohn (1949, p. 292, analysis A) gives an average of 0·27 per cent K in limestones. In the non-calcareous members of the Arahura series the element ranges from 0·73 to 4·48 per cent (Pettijohn, 1949, p. 250, 1·66 per cent). These figures indicate a considerable proportion of potassium feldspar in the original sediment. Since calcium is in general lower than the average for greywacke, if the sediments were derived mainly from igneous rocks, these were acidic rather than basic. While the formation of much illite is not likely under the depositional conditions, and hence adsorption by clay minerals will be a minor source, the detrital micas will add to the amount present. During metamorphism the element must be accommodated by the mica group, and comparison of Table 1 (mineral composition) with Table 5 indicates a correlation between the amount of biotite and muscovite and the potassium content.

Barium is present at low concentrations in the calcareous rocks, and is probably contained in admixed argillaceous material. In the non-calcareous Arahura rocks, it ranges from 450 to 1500 p.p.m. (Rankama and Sahama, 1950, p. 482, sandstones 170 p.p.m., shales 460 p.p.m.). Because of its large size and low ionic potential, barium is strongly adsorbed by clays, while precipitation as sulphate further depletes the available supply in sea-water. Hence limestones and sandstones

contain little of the element. Alkali feldspar has been reported to contain amounts as high as 9000 p.p.m. (Rankama and Sahama, 1950, p. 472), and since the barium content of plagioclase is commonly low (*loc. cit.*) the concentration of the element in the quartz-albite-biotite schists is supporting evidence for a large amount of unweathered alkali feldspar in the original sediment.

## The Nature of the Parent Rocks.

The chemical composition of the quartz-albite-biotite schists of the Arahura series shows close similarity, both for major and trace elements, to greywacke.

It is possible that metasomatic processes might alter a parent material so as to give a "greywacke" composition. In the Arahura rocks, boron and sodium are the only elements which might be taken to indicate metasomatism, but alternative explanations (boron from the original sediments, sodium from unweathered feldspar) are available.

Another possibility is that isochemical metamorphism has set up compositional gradients, and has resulted in large-scale redistribution of both the major and trace elements of the parent material (Turner, F. J., in Ahrens, 1954, p. 815.). In this case, after metamorphism, primary element variations would be obliterated and replaced by a new distribution pattern, although the overall composition of the original formation would remain the same. It should be noted that this effect is of a different order of magnitude (Turner, F. J., in Ahrens, 1954, p. 816, mentions disturbances of 1500 ft) from the long-recognized migration of elements over a few centimetres by metamorphic differentiation (Turner, 1948, p. 144.).

However, in the case of the Arahura rocks, there is strong field and petrological evidence of derivation from greywacke-type sediments. The fact that the chemical analyses of individual samples support the same conclusion may be interpreted as indicating that metamorphic processes, while producing a completely recrystallized rock, have not in this case altered the primary-element distribution to any appreciable extent. At most they have caused migration of major and trace elements over distances of a few centimetres.

The Arahura quartz-albite-biotite schists are thus considered to be derived from greywackes and associated sedimentary types, including minor calcareous beds. The original sediment seems to have contained much unweathered material, more alkali feldspar than plagioclase, and clay-mineral formation seems to have been at a minimum; for the distribution of the elements does not resemble that of shales. Neither does the amount of resistates appear to have been high.

From the regional extent of rocks of this age in New Zealand, they are generally considered to have been deposited in a major geosyncline. Under the conditions of formation of these "poured-in" types of sediments, chemical weathering is at a minimum, and sorting operates only to a minor degree. Such factors as ionic potential and pH hardly affect the presence or absence of trace elements contained in, for example, mechanically weathered feldspar poured into a geosynclinal trough and rapidly covered by more sediment. Even the effect of biogeochemical processes is at a minimum, as the general unfossiliferous character of greywackes attests.

Where the sediment is of this type, the distribution of the elements becomes to some degree fortuitous, depending on the source of supply.

A true picture of the average composition of a formation, such as the Arahura series, is only obtained by widespread sampling over many square miles. No attempt is made here to state an average composition for the Arahura quartz-albite-biotite schists on the basis of the figures reported in the Tables. The main reason for the analysis of the Arahura rocks was to see what chemical contrasts they offered to the enclosed Pounamu green schists. Hence, samples were collected with the idea of establishing what compositional limits might be expected in a representative section, for comparison with the green schists dealt with in the next section.

## The Distribution of the Elements in the Green Schists (Pounamu series)

The differences in chemical composition (Tables 5 and 6) between the quartz-albite-biotite (Arahura) schists, described in the preceding section, and the green schists (Pounamu series), reflects the variations in mineralogy (Tables 1 and 3). The differences in mineral composition are not due to any difference in metamorphic grade in the Pounamu rocks, for these are enclosed within the Arahura quartz-albite-biotite schists, so that all the minerals have developed under the pressure-temperature conditions of the albite-epidote-amphibolite facies. The green schists (Pounamu series) may be separated into two distinct chemical groups. The first comprises samples T-6, T-7, and T-9, and the second, samples T-12, T-13, T-14, and T-15. These groupings are also distinct in the field (Fig. 1). The first three samples are from separate bands of green schist each about 10 ft thick, and separated by quartz-albite-biotite schist. The second group is from a massive bed about 300 ft thick.

Since the green schists have been held by most authors to have originated through metamorphism of basic and ultrabasic igneous rocks, it is of interest here to compare the Pounamu figures with Barth's average rock types (1952, Table 33). Comparisons are also made with the Ontario diabase (Fairbairn, Ahrens, and Gorfinkle, 1953, pp. 42–46) and with the various Hawaiian basalts reported by Wager and Mitchell (1953, Tables 1 and 2).

Phosphorus, present in all the rocks, is higher in the first group. Igneous rocks with similar amounts of the element are rhyolites (350 p.p.m.), and dunites (220 p.p.m.) (Barth, 1952, Table 33). All other igneous rocks contain significantly higher amounts. Sample T-6 with 2100 p.p.m. may be compared with the average of 1950 p.p.m. for basalts (Barth, 1952).

Silicon averages 25·1 per cent (53·7 per cent $SiO_2$) in the first group and 23·8 per cent (50·9 per cent $SiO_2$) in the second. (Barth, 1952, gabbro 22·5 per cent = 48·2 per cent $SiO_2$, basalt 22·9 per cent = 49·1 per cent $SiO_2$).

Aluminium is somewhat higher in the first group (7·7 per cent) compared with the second (5·6 per cent). The first is similar to Barth's basalt (8·3 per cent) and the second to the Hawaiian picrite basalts (Wager and Mitchell, 1953) which average 4·9 per cent.

Chromium is one of the more significant elements. In the rocks of the first

*Table 6. Analyses of the green schists (Pounamu series) (expressed as parts per million)*

| | First group | | | Second group | | | |
|---|---|---|---|---|---|---|---|
| | T-6 | T-7 | T-9 | T-12 | T-13 | T-14 | T-15 |
| $P^{5+}$ | 2000 | 450 | 590 | 570 | 220 | 160 | 270 |
| $Si^{4+}(\times 10^3)$ | 25·6 | 25·0 | 24·7 | 23·9 | 26·4 | 24·7 | 20·1 |
| $Al^{3+}$ | 59500 | 75000 | 97800 | 64800 | 50800 | 61100 | 45600 |
| $Cr^{3+}$ | 310 | 235 | 560 | 2900 | 2200 | 1350 | 1550 |
| $Fe^{3+}$ | 70600 | 52100 | 64800 | 78000 | 67100 | 45300 | 47700 |
| $Mg^{2+}$ | 42000 | 56000 | 30500 | 86000 | 61800 | 47500 | 53000 |
| $Ti^{4+}$ | 3900 | 3900 | 7100 | 1300 | 280 | 260 | 200 |
| $Ni^{2+}$ | 200 | 160 | 160 | 530 | 360 | 250 | 225 |
| $Co^{2+}$ | 54 | — | 57 | 71 | 50 | 51 | 51 |
| $Cu^{2+}$ | — | — | 270 | 220 | 60 | 26 | 33 |
| $V^{3+}$ | 280 | 120 | 130 | 145 | 110 | 75 | 88 |
| $Zr^{4+}$ | 160 | 65 | 140 | — | — | — | — |
| $Mn^{2+}$ | 2500 | 1200 | 1400 | 1700 | 1500 | 1600 | 2100 |
| $Sc^{3+}$ | — | — | 25 | 35 | 30 | 20 | 20 |
| $Y^{3+}$ | 20 | 20 | 20 | — | — | — | 20 |
| $Na^{+}$ | 17100 | 48500 | 12500 | 5500 | 7100 | 11100 | 3100 |
| $Ca^{2+}$ | 69800 | 37100 | 69000 | 64100 | 72400 | 75500 | 128000 |
| $Sr^{2+}$ | 87 | 27 | 210 | 22 | 80 | 43 | 43 |
| $K^{+}$ | 3500 | 4200 | 11400 | 7400 | 2300 | 1800 | 2000 |
| $Ba^{2+}$ | 25 | — | 125 | 18 | 10 | 10 | 14 |

The following elements were not present above the minimum detectability (in brackets): B (30), Be (100), Ge (25), Mo (50), Sn (50), La (100), Pb (50). — : not detected. Analyst: S. R. Taylor.

group it averages 370 p.p.m., but in those of the second group 2000 p.p.m., while in the Arahura schists it never exceeds 150 p.p.m. (Wager and Mitchell, 1953, picrite basalt 1700 p.p.m., basalt 470 p.p.m.; Fairbairn *et al.*, 1953, Ontario diabase 220 p.p.m.). Chromium is strongly enriched in basic and ultrabasic rocks, and the amount of this element in the green schists is a strong indication of parental basic igneous rock. It is also of interest to note the steady decrease in samples T-12, T-13, and T-14. These samples are at increasing distances from the contact with the Arahura series. This trend is observable in the following elements: phosphorus, iron, magnesium, titanium, nickel, cobalt, copper, vanadium, and scandium, while sodium and calcium increase steadily in the same sequence. These facts are commented upon in the next section.

The iron content of the first group is 6·3 per cent, and of the second, 6·0 per cent (Barth, 1952, basalt 8·7 per cent).

Magnesium is lower in the first group (4·3 per cent) than in the second (6·2 per cent) (Barth, 1952, basalt 3·7 per cent; Wager and Mitchell, 1953, picrite basalt 11·4 per cent, basalt 4·6 per cent).

As is commonly the case in igneous rocks, the distribution of titanium parallels that of phosphorus, being lower in the second group (T-12, T-13, T-14, T-15) where it also shows a significant steady decrease similar to that shown by chromium.

This again emphasizes the more basic character of the main green schist belt, for titanium is enriched in basalts compared with earlier or later rocks in a crystallization differentiation series.

Nickel follows chromium. It is present at 340 p.p.m. in the main green schist belt, but at 170 p.p.m. in the first group (T-6, T-7, T-9) (Fairbairn *et al.*, 1953, picrite basalt 1000 p.p.m., basalt 80 p.p.m.).

Cobalt was not detected in T-7 (<10 p.p.m.), but is present elsewhere in rather uniform amounts, averaging 55 p.p.m. but reaching 71 p.p.m. in T-12. (Fairbairn *et al.*, 1953, Ontario diabase 40 p.p.m.; Wager and Mitchell, 1953, picrite basalt 70 p.p.m., basalt 33 p.p.m.) The three elements, chromium, nickel, and cobalt, in the green schists all show close correspondence to their distribution in basic igneous rocks.

Copper shows in the main green schist belt a decrease away from the contact, dropping from 220 p.p.m. in T-12 to 26 p.p.m. in T-14. (Fairbairn *et al.*, 1953, Ontario diabase 90 p.p.m.; Wager and Mitchell, 1953, picrite basalt 150 p.p.m., basalt 170 p.p.m.)

Vanadium averages 175 p.p.m. in the first group and 105 p.p.m. in the second (Fairbairn *et al.*, 1953, Ontario diabase 220 p.p.m.; Wager and Mitchell, 1953, picrite basalt 250 p.p.m., basalt 300 p.p.m.). It is not notably different in abundance in the Arahura rocks. It would not seem to be a particularly useful element for indicating an igneous as opposed to a sedimentary origin of metamorphic rocks, although its absence might indicate derivation from acidic differentiates (see, however, Rankama and Sahama, 1950, p. 602).

Zirconium averages 120 p.p.m. in the first group, but was not detected in the second (Fairbairn *et al.*, 1953, Ontario diabase 100 p.p.m.; Wager and Mitchell, 1953, picrite basalt 70 p.p.m., basalt 100 p.p.m.). The distribution of this element again emphasizes the different geochemical environment of the Arahura and Pounamu rocks, for in the former, zirconium is rather evenly distributed.

Manganese shows no significant variation between the two groups, averaging 1700 p.p.m. for the series (Barth, 1952, basalt 2400 p.p.m.). It is generally higher and more evenly distributed than in the Arahura series.

Scandium ranges from <20 p.p.m. to 35 p.p.m. in the main green schist belt (Fairbairn *et al.*, 1953, Ontario diabase 35 p.p.m.; Wager and Mitchell, 1953, basalt 10 p.p.m.). It displays the tendency to be enriched in the most basic rocks, for while it is present throughout the second group, it occurs only in T-9 in the first. It should be mentioned here that T-9 is the most basic rock of the first group, containing the highest chromium, cobalt, copper, and scandium.

Yttrium shows its usual tendency to occur in the less basic rocks.

Sodium is somewhat variable, but is consistently higher in the first group, while reaching quite low values in the second. Samples T-12, T-13, and T-14 show a steady increase.

Excluding the calcareous members of the Arahura series, calcium is present in the green schists in much greater amounts. Metamorphic differentiation has again affected the distribution of calcium in individual samples. After the subtraction of the necessary amounts for hornblende, clinozoisite, and epidote,

and the small amount required for albite with 5 per cent An component, the excess has crystallized as calcite, no doubt owing to the lack of aluminium and silicon to form further amounts of these minerals. The calcium figures are similar to those found in basic rocks (Barth, 1952, basalt 6·4 per cent). The element parallels sodium in samples T-12, T-13, and T-14. The high figure for T-15 may be due to some assimilation of the adjacent limestones.

In the Pounamu green schists, strontium is present in the low amounts typical of basic rocks, and contrasts with the higher amounts in the Arahura quartz-albite-biotite schists.

Potassium is also present at low values similar to its abundance in basic rocks (Barth, 1952, gabbro 7400 p.p.m.; Fairbairn *et al.*, 1953, Ontario diabase 1·0 per cent; Wager and Mitchell, 1953, picrite basalt 3200 p.p.m., basalt 3500 p.p.m.), and controls the low biotite content of the Pounamu rocks compared with the Arahura series.

Barium is quite low in the series and the Arahura rocks are much higher. The distribution of barium and strontium is typical of basic rocks.

## The Origin of Green Schists

A consideration of the data presented in Table 6 and discussed in the previous section shows that the rocks may be separated into two distinct groups, mainly on the basis of trace-element distribution. The first group comprises samples T-6, T-7, and T-9, and the second T-12, T-13, T-14, and T-15. These rocks are also separable in the field and on mineralogical grounds. In general, the distribution of the chemical elements, making due allowance for the migration of ions during metamorphism, bears a close similarity to that found in basic igneous rocks, and is quite distinct from the distribution of the elements in the Arahura quartz-albite-biotite schists. The Pounamu (green schists) series contain significantly greater amounts of chromium, magnesium, nickel, cobalt, and copper, and significantly lower amounts of phosphorus, titanium, strontium, barium, and potassium (and sodium and zirconium in the second group).

The first group (T-6, T-7, and T-9), which forms small bands in the Arahura series, has, as shown in the preceding section, a similar major and trace-element content to that found in basalts. The main green schist belt (T-12, T-13, T-14, and T-15) is considered to be derived from quite basic but not ultrabasic igneous rocks. The trace-element distribution would fit either a picrite- or olivine-basalt as defined by Macdonald (1949, pp. 1544–1549); the trace-element distribution of which has been reported by Wager and Mitchell (1953).

Sample T-12, one foot above the contact with the Arahura series, contains 60 per cent hornblende; sample T-13, 10 feet above, has 40 per cent; and T-14, 3 per cent. Thus there is an amphibole concentration, decreasing away from the contact. These amphibole-rich layers in green schists have been described from many localities, notably Schuyler, Virginia (Hess, 1933), Western Otago, New Zealand (Hutton, 1940), and Unst, Shetland Islands (Read, 1934). While the igneous origin of these green schists has not been in doubt (although green schists of sedimentary origin are known; Tilley, 1938), the origin of the amphibole-rich layers has been less certain. Hess (1933) appealed to water and carbon dioxide,

emanating from an acid intrusion to alter the Virginian gabbros to amphibolites. The widespread occurrences of small bands of green schists throughout Otago and Westland, and the apparent lack of effects in adjacent rocks and of an apparent source for the solutions, are strong objections. However, carbonate schists are rather common adjacent to green schists in Westland, a fact commented upon by Wellman (1952, p. 23).

Hutton (1940, pp. 54–55), in dealing with the extensive chlorite zone of the Otago schists (of which the Alpine Schist Belt is a continuation), considered that the amphibole segregations of green schists of basic igneous parentage were the result of metamorphic differentiation. In some rocks, relict brown hornblende was observed altering to actinolite, and in these cases he thought it possible that the parental material was a gravitationally differentiated hornblende layer in basalt. The Pounamu schists have reached a higher grade of metamorphism than those described by Hutton, and relict structures are absent. It should be noted that the bulk analysis of the amphibole layers shows appreciable nickel and chromium (Hutton, 1940, p. 55). The possibility that the green schists are derived from hornblendic or pyroxenic igneous rocks may be ruled out on the compositional ground stated earlier. Undoubtedly all these factors operate in different cases; some amount of metamorphic differentiation is probably common to all, and it has caused some segregation in both the Arahura and Pounamu series.

New light is thrown on the problem by a study of the distribution of the elements in samples T-12, T-13, and T-14. Sample T-15 is close in composition to T-14, but as it is separated by 250 ft of inaccessible section, it is not included in the discussion. In Fig. 2 are plotted the data for phosphorus, chromium, iron, magnesium, titanium, nickel, cobalt, copper, vanadium, scandium, sodium, and calcium. The last two elements show a steady rise, but all the others show a more or less pronounced drop. Also in Fig. 2 are shown data for the Hawaiian petrographic province (Wager and Mitchell, 1953), the Braefoot outer sill (Higazy, 1952), and the Skaergaard intrusion (Wager and Mitchell, 1951). The general trends for these localities, widely separate in space, size, and time, are remarkably similar. Chromium, iron, magnesium, nickel, cobalt, sodium, and calcium show identical trends, vanadium and scandium are similar, while copper and titanium in the earlier stages of the Skaergaard rocks are similar to the Pounamu green schists. The weight of evidence makes a common cause reasonable, and it is therefore suggested that samples T-12, T-13, and T-14 owe their composition to crystal fractionation and, indeed, that they represent a layered sill produced by gravitational differentiation.

This interpretation leads to the conclusion that the bottom of the whole sequence is to the south-east, and that the beds are thus overturned (Fig. 1.) It also indicates that the enclosing Arahura series must have been close to horizontal at the time of the intrusion, and that the igneous activity was therefore prior to the major deformation as well as metamorphism.

## Conclusions

The distribution of both major and trace elements in the quartz-albite-biotite schists of the Arahura series indicates that the chemical composition of the

original greywacke sediment has not changed to any appreciable extent during metamorphism. This conclusion is reinforced by the clear chemical evidence of basic igneous rock parentage of the green schists (Pounamu series), and in particular by the persistence of a primary, uneven element distribution due to igneous processes.

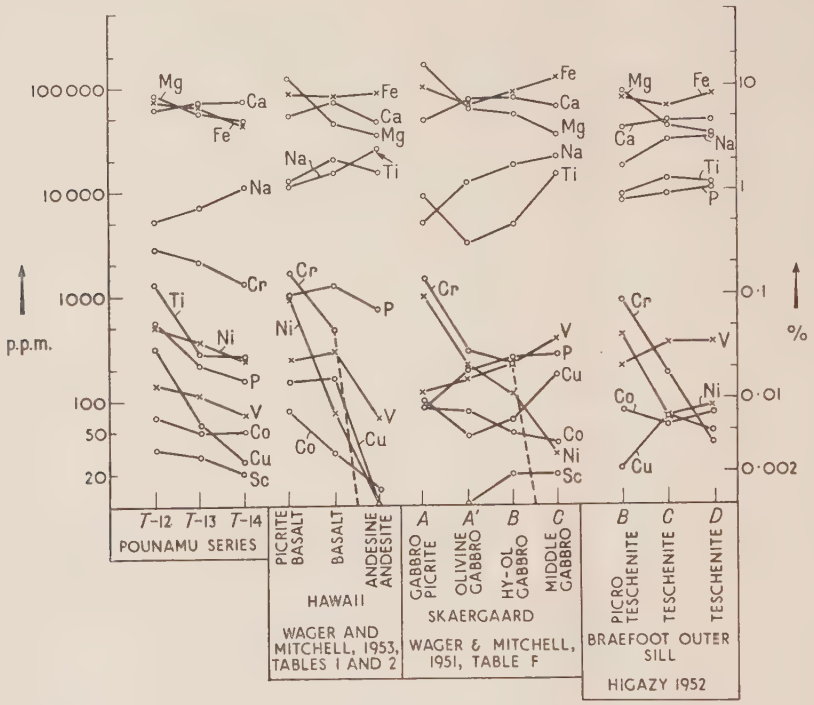


Fig. 2. A comparison of the variation of Ca, Co, Cr, Cu, Fe, Mg, Ni, P, Na, Sc, Ti, and V in samples T-12, T-13, and T-14 of the Pounamu green schists, with certain data from the Hawaiian petrographic province, the Skaergaard intrusion, and the Braefoot outer sill.

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# Metamorphism of natural waters in the crust of weathering—3*

I. I. Chebotarev
Australia

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## Discussion of the Results

### *General approach*

The perplexing nature of the problem in question involves many aspects of the consideration. Among the geological problems the geologic history of the region, structural relations, lithology and facies of the sediments, their mineralogical composition and thickness, areal extent, post-depositional factors, etc., are of understandable significance.

The hydrological approach requires the consideration of the recharge-discharge cycle of subterranean waters; the water-exchange conditions in the subsurface reservoir; the physical properties of the water-bearing formations; the hydraulics of the aquifer, that is, the hydraulic gradients, velocity of flow, storage capacity, water-yielding ability, static, dynamic, and perpetual water resources, etc.

The chemistry of water involves the consideration of the fundamental geochemical principles upon which our knowledge of the earth's crust is based; the consideration of the phases, cycles, and the types of the products of weathering; the geochemical properties of the ions and compounds; the modification of the salinity concentration of water in the various thermodynamic environment and hydraulic conditions, etc.

The naturalist who is aware of the cycloidal migration of the chemical elements in the earth's crust realizes that the subterranean waters of different chemical

* Part 1—*Geochim. et Cosmochim. Acta* **8**, 22; Part 2—*ibid.* 137.

*Table 58. Hydrodynamic zones and geochemistry of subterranean waters in the crust of weathering*

| Hydrodynamic zones | | Geochemistry of water | | | | Geological environment | | | Examples |
|---|---|---|---|---|---|---|---|---|---|
| *Recharge-discharge cycle* | *Water-exchange* | *Classes* | *Hydrochemical facies* | *Approximate salinity (p.p.m.)* | *Common terms for water* | *Structures* | *Relation to water* | *Depth (feet)* | |
| Zone of recharge | Active exchange | I and II (sometimes III) | Low saline facies | 180–2,400 | Fresh | Different | Intensive flush | Usually less than 500 | Everywhere |
| | | | Transitional (typical) facies | 2,400–11,400 | Brackish | Deep portions of structures with peculiar geochemical environment | Delayed flush | Sometimes 5,000–7,000 | Great Artesian Basin, Rocky Mountain oilfield and others |
| | | | High saline facies | 11,400–37,800 | Saline | | Hampered flush | | |
| Zone of pressure | Delayed exchange | III and IV | Low saline facies | 400–2,500 | Fresh | Different | Inadequate flush | Usually less than 1,000 | Everywhere |
| | | | Transitional (typical) facies | 2,500–7,400 | Brackish | Deeper portions of structures, folded zones | Circulation and drainage limited | Sometimes 3,000–4,000 | Pre-Caucasian Basin, South Dakota Basin, some oilfield areas |
| | | | High saline facies | 7,400–19,300 | Saline | | | | |
| Zone of accumulation | Stagnant conditions | V | Low saline facies | 1,500–20,000 | Fresh and saline | Different | Salt accumulation prevails upon leaching | Different | Chiefly in arid regions; deeper portions of many artesian basins; some oilfields |
| | | | Transitional (typical) facies | 20,000–90,000 | Saline and brines | Deeper portions of structures, highly folded zones | | Sometimes 8,000–13,000 | |
| | | | High saline facies | 90,000–300,000 | Brines | | Water exchange manifests on geological scale time | | Many oilfield areas (Louisiana, Alberta, etc.) |

composition ranging from dilute to almost saturated has appeared in the subsurface reservoir not at once, but their salinity is resulted by a set of factors which operate either in a certain sequence or their combined effect has caused eventually the occurrence of water of the various chemical types.

It can be ascertained that there are definite local and regional (vertical and horizontal) hydrodynamic, hydrochemical, geothermal, and gaseous zoning in the distribution of subterranean waters in the earth's crust.

In Oklahoma-Kansas region, for instance, a very important correlation between the salinity concentration in water and the geological structure has been found (Case, 1934).

It has been definitely proved in this study that there is a well manifested relationship of the hydraulic gradients and salinity of water (Tables 14–17); the increase in the salinity concentration becomes apparent as the water-exchange condition deteriorates with depth (Tables 18, 19, 20, 21); the salinity of subterranean water substantially increases with distance from the intake area (Tables 22, 23), with the approach to the sea (Table 24), with the time of flow, etc.

### *Hydrodynamic zones and geochemistry of water*

The analysis of the data related to the recharge-discharge of subterranean waters enables us to allot the three principal hydrodynamic zones in the crust of weathering, namely:—

(1) Zone of active exchange,
(2) Zone of delayed exchange, and
(3) Zone of stagnant conditions.

The relationship of these zones to the geochemistry of water and the geological environment is summarized in Table 58 and Fig. 18.

### *Correlation*

The data represented in the preceding chapters and related to the geochemistry of subterranean waters of the different types provide a basis for the correlation of water associated with the different geological formations (Table 59).

*Table 59. Typical salinity (50 per cent frequency) of subterranean waters from different geological formations (correlative table)*

| *Formation* | *Region* | *Total salinity (p.p.m.)* | *Number of analyses* | *Reference* |
|---|---|---|---|---|
| Recent-Pleistocene | Europe | 1,350 | 616 | Table 45 |
| Tertiary | Europe | 3,827 | 993 | Table 47 |
| Tertiary | Australia | 3,680 | 592 | Table 48 |
| Mesozoic | Europe | 2,084 | 105 | Table 50 |
| Paleozoic | South Africa | 588 | 161 | Table 52 |
| Metamorphic | South Africa | 640 | 88 | Table 54 |
| Igneous | Europe | 650 | 314 | Table 56 |
| Igneous | South Africa | 648 | 175 | Table 57 |
| — | — | Total | 3,044 | — |

### *Depth to water*

It is assumed that subterranean water occurs in the crust of weathering as far down as to a point where no pores, fractures, cavities, and other openings could persist in sedimentary rocks under the great load of the superincumbent strata and temperature.

However, the absence of water due to the unusual local geological conditions in some formations is also known (Reeves, 1917).

It was held (Adams, 1912) that under the conditions of pressure and temperature which are believed to be present within the earth's crust, empty cavities may exist in granite to a depth of at least eleven miles.

The conclusion has also been drawn that "oil and gas may occur in sandstones down to a depth of 65,620 feet and in limestones to 51,300 feet" (Cloninger, 1950).

These concepts would make it possible for subterranean water to be found at a much greater depth than we know at present.

In oilfields the deepest known waters belong to the chloride type, which are found at a depth over 11,000 feet (Table 32), although the depth of their occurrence varies considerably.

Bicarbonate waters occur at much more shallow depth, but the variation in depth is still great.

Sulphate waters, as it has been stated (Chebotarev, 1952), are actually of a transitional type; they occur at still more shallow depth, although the range of depth is still significant.

Taking into account the types of subterranean waters and the relationship of the different ingredients found in subterranean waters, it can be assumed that the relative mobility of the chemical element soluble in water can be broken at the depth of 5,000 to 7,000 feet.

### *Salinity variation*

*Regularities*

As it has been shown, salinity of subterranean waters varies with the change of the hydraulic gradients as well as with depth of occurrence of subterranean waters, and with the distance from the outcrops of the water-bearing bed.

Actually the salinity distribution of subterranean waters is a regional phenomenon dependent on a set of factors such as the mobility of the chemical elements, hydrodynamic conditions in the subsurface reservoirs, and the local geochemical environment of the area.

Subterranean waters cannot remain unchanged in chemical composition so long as they are in contact with the rocks containing soluble material, and the water is not already saturated.

The chemical composition of waters is in fact a result of prolonged leaching of sedimentary beds by moving water sometimes covering a vast span of time.

In other words, the keynote of the chemical alteration of subterranean waters is their adoption of the local geological conditions.

The structure of the rocks controls the amount of water, its distribution and motion in the subsurface reservoir.

Countless minor joints and cracks are often the principal channels of vertical migration of water.

The salinity concentration of water usually increases down-dip, and the smaller the intake area and the more hampered the drainage the more rapid is the rate of increase in salinity of subterranean waters.

*Coefficient of variation* ($C_v$)

As a mathematical characteristic $C_v$ can be considered a reliable criterion for the estimation of the salinity variation of the major geochemical groups of subterranean waters as well as those associated with the different formations.

The following four categories of salinity variation may be allotted:

Low variation with $C_v < 0{\cdot}5$.

Moderate variation with $C_v = 0{\cdot}5 - 1{\cdot}0$.

Great variation with $C_v = 1{\cdot}0 - 1{\cdot}5$.

Very great variation with $C_v > 1{\cdot}5$.

The data in Table 60 illustrate the magnitude of $C_v$ of the different occurrences of water.

*Table* 60. *Coefficient of variation* ($C_v$) *of the salinity distribution in subterranean waters*

| *Type of water* | $C_v$ | | | | | | | *Reference* |
|---|---|---|---|---|---|---|---|---|
| | *Total salinity* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | |
| *Major groups* | | | | | | | | |
| Bicarbonate | 1·2 | 1·1 | 0·8 | 0·6 | 1·2 | 0·8 | 0·9 | Table 33 |
| Sulphate | 0·9 | 0·9 | 0·7 | 0·9 | 1·0 | 0·6 | 0·8 | Table 36 |
| Chloride | 1·0 | 1·1 | 1·2 | 1·0 | 0·9 | 0·8 | 1·1 | Table 37 |
| *Other occurrences* | | | | | | | | |
| Kentucky brines | 0·6 | — | — | — | — | — | — | Table 40 |
| Metalliferous deposits | 1·3 | — | — | — | — | — | — | Table 44 |
| Recent-Pleistocene (Australia) | 1·9 | — | — | — | — | — | — | Table 46 |
| Tertiary (Europe) | 0·5 | 1·0 | 1·0 | 0·9 | 0·5 | 0·9 | 0·5 | Table 47 |
| Tertiary (Australia) | 0·5–0·6 | — | — | — | — | — | — | Table 48, 49 |
| Mesozoic (Europe) | — | — | — | — | 2·0 | 0·9 | — | Table 50 |
| Paleozoic (Europe) | — | — | — | — | 0·6 | 0·9 | 0·5 | Table 51 |
| Paleozoic (South Africa) | 0·9 | — | — | — | — | — | — | Table 52 |
| Pre-Cambrian (Australia) | 0·5 | — | — | — | — | — | — | Table 55 |

Thus, the sulphate waters can be characterized as being of moderate salinity variation, while both the bicarbonate and chloride waters belong rather to the category of great variation.

The Tertiary waters have low variation of the total salinity, but most of the ions vary considerably.

Kentucky brines are fairly uniform in their salinity concentration, but subterranean waters associated with the metalliferous deposits are of the extreme variability.

## *Metamorphism of waters*

### *Chemical relationship of major groups*

Because of the different mobility of the chemical elements and the nature of the physical-chemical processes in the subsurface reservoir, the geochemical types of water change with the increase of the total salinity as well as with increasing depth, and the following series hold good:

$$HCO_3' \rightarrow HCO_3' + Cl' \rightarrow Cl' + HCO_3' \rightarrow Cl' + SO_4'' \quad \text{or} \quad SO_4'' + Cl' \rightarrow Cl';$$

This sequence is correct in vertical zones as well as in the horizontal zones of subterranean waters.

The two main stages of metamorphisation of natural waters can be recognized: the *normal* course and *reverse* course.

The former may be represented in the following manner:

Bicarbonate waters → bicarbonate-chloride waters → chloride-bicarbonate waters

→ chloride-sulphate (or sulphate-chloride waters) → sulphate waters → chloride waters

The latter may be represented by the major geochemical groups of waters as follows:

Bicarbonate waters ← sulphate waters ← chloride waters

Although the ions which have been laid down as a basis for the geochemical classification of water are considered to be present in a state of dissociation, the equilibrium of the saline matter dissolved in water as a certain physical-chemical system can be characterized by the binding of anions and cations into salts.

The more soluble salts are mainly those of sodium sulphate, sodium carbonate or bicarbonate, sodium chloride, magnesium, potash, etc.

According to the Bunsen-Fresenius conception, the ions of the strong acids ($Cl'$, $SO_4''$) form a chemical combination with alkalies ($Na^{\cdot}$, $K^{\cdot}$) and the rest of the acid radicles give a combination with the alkaline earths ($Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$). If the latter are in surplus in water they will combine with the weak acids ($CO_3''$, $HCO_3'$) (Chebotarev, 1952).

The assumed composition of salts in waters of the major geochemical groups is given in Table 61.

Thus, the main equilibrium-systems characteristic for the physical-chemical processes in waters of various types are as follows:

BICARBONATE WATERS—

$$NaHCO_3 \text{ (and } Na_2CO_3)—NaCl—Na_2SO_4—H_2O \text{ ;}$$

SULPHATE WATERS—

$$Na_2SO_4—NaCl—MgSO_4—H_2O \text{ ;}$$

$$(2NaCl + 2MgSO_4 \rightleftarrows Na_2SO_4 + MgCl_2) \text{ ;}$$

CHLORIDE WATERS

$$NaCl—CaCl_2—MgCl_2—H_2O \text{ ;}$$

*Table* 61. *The assumed composition of salts in typical waters of the major geochemical groups* (*from Table* 38)

| *Bicarbonate* | | | | *Sulphate* | | | | *Chloride* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Ions* | | *Compounds* | | *Ions* | | *Compounds* | | *Ions* | | *Compounds* | |
| *Ingredients* | *Reacting value %* | *Salts* | *Reacting value %* | *Ingredients* | *Reacting value %* | *Salts* | *Reacting value %* | *Ingredients* | *Reacting value %* | *Salts* | *Reacting value %* |
| Na + K | 46·6 | NaCl | 30·0 | Na + K | 33·5 | NaCl | 23·2 | Na + K | 34·3 | NaCl | 68·6 |
| Ca | 1·3 | $Na_2SO_4$ | 9·2 | Ca | 11·5 | $Na_2SO_4$ | 43·8 | Ca | 12·4 | $CaCl_2$ | 24·8 |
| Mg | 2·1 | $NaHCO_3$ | 54·0 | Mg | 5·0 | $MgSO_4$ | 10·0 | Mg | 3·3 | $MgCl_2$ | 2·8 |
| Cl | 15·0 | $Ca(HCO_3)_2$ | 2·6 | Cl | 11·6 | $CaSO_4$ | 13·0 | Cl | 48·1 | $MgSO_4$ | 2·2 |
| $SO_4$ | 4·6 | $Mg(HCO_3)_2$ | 4·2 | $SO_4$ | 33·4 | $Ca(HCO_3)_2$ | 10·0 | $SO_4$ | 1·1 | $Mg(HCO_3)_2$ | 1·6 |
| $HCO_3$ | 30·4 | | | $HCO_3$ | 5·0 | | | $HCO_3$ | 0·8 | | |
| Total | 100·0 | — | 100·0 | — | 100·0 | — | 100·0 | — | 100·0 | — | 100·0 |

By taking into account the relationship of these salts (VALIASHKO, 1939), the following characteristics ("coefficients of *metamorphisation*" $k_m$) of the geochemical conditions in each type of the waters may be found:

BICARBONATE WATERS

$$k_m = \frac{Na_2(K_2)CO_3 + Na(K)HCO_3}{Na_2SO_4} = 5{\cdot}8 ;$$

SULPHATE WATERS

$$k_m = \frac{Na_2SO_4}{MgSO_4} = 4{\cdot}4 ;$$

CHLORIDE WATERS

$$k_m = \frac{MgCl_2}{CaCl_2} = 0{\cdot}1 ;$$

*Coefficient of water exchange*

As it has been shown (Table 58), the hydrodynamics of subterranean waters, that is, the intensity of the water-exchange with the earth's surface, is an essential factor determining the salinity variation of waters.

The equilibrium of the chemical systems which are typical for the major geochemical group of waters can be considered as a criterion for the estimation of the water exchange conditions in the subsurface reservoir. This criterion may be termed *coefficient of water exchange* ($k_e$).

The following ratio has been introduced for the computation of this coefficient:

$$k_e = \frac{Na(K)HCO_3 + (Ca, Mg)(HCO_3)_2}{Na(K)Cl + (Ca, Mg)Cl_2 + Na_2SO_4 + (Ca, Mg)SO_4} ;$$

Thus (from Table 61):

| | | Absolute | Relative |
|---|---|---|---|
| BICARBONATE WATERS | $k_e =$ | 1·55 | 96·9 |
| SULPHATE WATERS | $k_e =$ | 0·11 | 6·9 |
| CHLORIDE WATERS | $k_e =$ | 0·016 | 1·0 |

It is apparent therefore that as the water-exchange conditions deteriorate, the geochemical type of water changes according to the aforementioned *normal* course of metamorphism of water.

*Ionic ratios*

The ionic ratios are illustrated by the data presented in Tables 62, 63, and 64.

The data presented in Tables 62 and 63 show the following relationship of the ionic ratios in the major geochemical groups of waters:

$\frac{Cl'}{Mg''}$ ratio. In all groups it decreases with the decrease of the salinity concentration, but the rate is quite different in all types: in the bicarbonate waters it is as great as 47 times, in the sulphate water —7·6 times, and in the chloride waters only 1·5 times.

*Table 62. Ionic ratios in subterranean waters of the major geochemical groups*

| Type of water | Ratios | Per cent frequency | | | | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | 99·0 | |
| Bicarbonate | $\frac{Cl'}{Mg^{\cdot\cdot}}$ | 24·00 | 15·40 | 11·90 | 7·10 | 3·60 | 1·10 | 0·51 | Table 33 |
| | $\frac{SO_4''}{Cl'}$ | 0·14 | 0·17 | 0·22 | 0·30 | 0·45 | 0·96 | 1·10 | Table 33 |
| | $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ | 0·88 | 0·61 | 0·66 | 0·62 | 0·50 | 0·33 | 0·19 | Table 33 |
| | $\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$ | 0·97 | 0·96 | 0·95 | 0·92 | 0·89 | 0·82 | 0·62 | Table 33 |
| Sulphate | $\frac{Cl'}{Mg^{\cdot\cdot}}$ | 3·36 | 3·02 | 2·71 | 2·32 | 1·50 | 0·69 | 0·44 | Table 36 |
| | $\frac{SO_4''}{Cl'}$ | 1·40 | 1·79 | 2·10 | 2·88 | 4·36 | 14·33 | 32·71 | Table 36 |
| | $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ | 2·14 | 1·85 | 1·90 | 2·30 | 2·19 | 3·65 | 6·50 | Table 36 |
| | $\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$ | 0·65 | 0·69 | 0·69 | 0·67 | 0·63 | 0·60 | 0·52 | Table 36 |
| Chloride | $\frac{Cl'}{Mg^{\cdot\cdot}}$ | 19·20 | 17·43 | 16·55 | 14·57 | 13·74 | 12·5 | 16·0 | Table 37 |
| | $\frac{SO_4''}{Cl'}$ | 0·018 | 0·020 | 0·020 | 0·023 | 0·025 | 0·029 | 0·035 | Table 37 |
| | $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ | 5·80 | 4·93 | 4·58 | 3·76 | 3·43 | 2·57 | 4·66 | Table 37 |
| | $\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$ | 0·66 | 0·67 | 0·67 | 0·68 | 0·69 | 0·71 | 0·66 | Table 37 |

*Table 63. Ionic ratios in typical waters of the major geochemical groups (50 per cent frequency)*

| *Types of waters* | $\frac{Cl'}{Mg^{\cdot\cdot}}$ | $\frac{SO_4''}{Cl'}$ | $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ | $\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$ |
|---|---|---|---|---|
| Bicarbonate | 7·10 | 0·30 | 0·62 | 0·92 |
| Sulphate | 2·32 | 2·88 | 2·30 | 0·67 |
| Chloride | 14·57 | 0·023 | 3·76 | 0·68 |
| Oceanic water | 5·08 | 0·10 | 0·20 | 0·79 |
| Relative mobility | 77·0 | 0·57 | 2·30 | — |

$\frac{SO_4''}{Cl'}$ ratio. Generally it increases with the decrease of salinity concentration of water; the rate of this change is as follows: in the bicarbonate waters 8 times, in the sulphate waters 23·3 times, and in the chloride waters only about 2 times.

$\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ ratio. It varies in different ways: while in the bicarbonate waters and in the chloride waters it decreases with the decrease of the salinity concentration (4·6 times and 2·2 times respectively), in the sulphate waters it gradually increases with the decrease of total salinity of water.

$\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$ ratio. It is remarkably similar in the sulphate waters and in the chloride waters, but it is of the higher content in the bicarbonate waters, due to the high solubility of sodium carbonate and bicarbonate salts.

In the representative analyses of subterranean waters of the various occurrences (Table 64), the ionic ratios vary considerably, depending chiefly on the local hydrodynamic and geochemical conditions, but the following facts deserve to be mentioned here:

While the ratios in the waters from geysers show great variation, the chemical analyses of waters (Table 42) suggest that the water discharged by the springs is largely dependent on the local supply; the $HCO_3$-ion content is particularly indicative in this respect.

Otherwise it has been recognized that the magmatic centre is the source of the heat, sulphur, $CO_2$, chlorine, and some other ingredients in the Steamboat Springs area, Nevada, while density and isotope studies indicate that in some hotter springs only 6 to 16 per cent of the water may be originated from the same source (Ingerson, 1954).

The ratios in the waters associated with the mud volcanoes are rather similar to

*Table 64. Ionic ratios in subterranean waters of the various occurrences*

| *Type of water* | $\frac{Cl'}{Mg^{\cdot\cdot}}$ | $\frac{SO_4''}{Cl'}$ | $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ | $\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$ | *Total salinity (p.p.m.)* | *Reference to Table* |
|---|---|---|---|---|---|---|
| *Volcanic association* | | | | | | 42 |
| *Geysers* | | | | | | |
| Geyser Beowawe, Nevada | — | 0·5 | — | 0·90 | 1,208 | |
| Steamboat Spring, Nevada | 385·00 | 0·13 | 7·0 | 0·92 | 2,596 | |
| Sulphur Bank, California | 2·85 | 3·0 | 0·57 | 0·70 | 8,245 | |
| *Mud volcanoes* | | | | | | 43 |
| Cheleken No. 2 | 224·00 | 0·02 | 0·50 | 0·99 | 43,360 | |
| Boyadag No. 5 | 25·00 | — | 4·10 | 0·79 | 265,000 | |
| Keimir No. 7 | 5·79 | 0·17 | — | 0·86 | 414,000 | |
| *Natural brines* | | | | | | 39 |
| Oil pool, Kansas | 11·25 | 0·008 | 1·52 | 0·77 | 55,000 | |
| Calcium work, Ohio | 3·57 | — | 2·43 | 0·04 | 76,100 | |
| Oil pool, Kansas | 7·92 | — | 0·57 | 0·80 | 150,400 | |
| Oil pool, Kansas | 15·62 | — | 2·29 | 0·77 | 250,000 | |
| Oil pool, Alberta | 25·00 | — | 10·5 | 0·49 | 300,000 | |
| Oil pool, Ohio | 21·49 | — | 2·39 | 0·84 | 425,900 | |
| *Mesozoic waters* | | | | | | 30 |
| *L. Cretaceous* | | | | | | |
| Patchawarra | 89·00 | 0·01 | 1·00 | 0·98 | 2,807 | |
| Nick O'Time | 10·90 | 0·07 | 3·05 | 0·65 | 31,992 | |
| *Jurassic* | | | | | | |
| Peachawarrina | 3·45 | 0·04 | 2·57 | 0·95 | 1,571 | |
| Oodnadatta | 2·75 | 0·30 | 0·21 | 0·70 | 2,167 | |
| *Paleozoic waters* | | | | | | 18 |
| Upper Permian | 0·14 | 2·28 | 3·82 | 0·06 | 332 | |
| Lower Permian | 2·29 | 0·47 | 1·01 | 0·61 | 482 | |
| Upper Carboniferous | 4·83 | 0·45 | 1·20 | 0·69 | 12,926 | |
| Middle Carboniferous | 9·17 | 0·03 | 1·20 | 0·76 | 118,291 | |
| Lower Carboniferous | 15·53 | 0·04 | 2·69 | 0·76 | 336,020 | |

those in all other natural brines except the water from Cheleken No. 2, where $\frac{Cl'}{Mg^{\cdot\cdot}}$ ratio is extremely high.

In natural brines $\frac{Cl'}{Mg^{\cdot\cdot}}$ and $\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$ ratios increase generally with the salinity concentration, but the latter varies in an irregular manner.

The $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ ratio is remarkable: in most of the representative analyses it corresponds with the relative mobility of the ions in the crust of weathering.

Thus, it can be stated that:

1. $\frac{Cl'}{Mg^{\cdot\cdot}}$ ratio follows the *normal* course of metamorphism of natural waters; its rate decreases with the deterioration of the water-exchange conditions (from the bicarbonate waters to the chloride waters).

2. $\frac{SO_4''}{Cl'}$ ratio normally increases in the sulphate waters.

The fall in concentration of $SO_4''$ in the presence of sulphate bacteria is known in some oilfields, and this process, which is due to the transition of sulphate ion into less oxidized anions as follow:

$$SO_4'' \rightarrow SO_3'' \rightarrow S_2O_3'' \rightarrow S''$$

may also reduce $\frac{SO_4''}{Cl'}$ ratio.

3. $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ ratio is probably the most instructive: it is of the lower magnitude in the bicarbonate waters and of the higher rate in the chloride waters, being chiefly caused by the hydraulics of underground flow.

It is, however, noteworthy that this ratio in the typical sulphate waters equals exactly 2·3, that is, to the relative mobility of these ions in the crust of weathering.

4. $\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$ ratio decreases with the deterioration of the water-exchange conditions.

5. The relationship of the ionic ratios in subterranean waters and particularly in those of the chloride type (including natural brines) to the ionic ratios in the oceanic waters clearly indicates that no similarity in their chemical composition can be recognized.

The ionic ratios in the bicarbonate waters seem to be akin to the oceanic water, but their chemical composition and association with the zone of the active water-exchange has nothing in common with the oceanic water.

It is therefore a moot point whether there are in the crust of weathering any of the so-called "connate" waters which have never been metamorphosed to some degree.

It has been stated, for instance, that in California Basin sediments "chloride maintains a constant concentration in the interstitial water with depth of burial, whereas sulphate decreases with depth" (Emery and Rittenberg, 1952).

## Cycle of Metamorphism of Natural Waters

As a result of the present study the following concept can be formulated:

1. Natural waters in the crust of weathering are an integral part of the hydrosphere and they take a part in the general circular motion of water in nature.

2. The hydraulics of subterranean waters, that is, the rate of the gradients and velocity of underground flow, are a factor of the decisive importance in the salinity variation of waters.

3. The amount of water in the subsurface reservoirs and its dynamics, that is, the intensity of the water-exchange with the earth's surface (active exchange,

Fig. 18. Cycle of metamorphism of natural waters in the crust of weathering.

delayed exchange, stagnant conditions) along with the relation of the water-bearing bed to water (e.g., intensive flush, hampered flush, salt accumulation) and drainage conditions, result in the salinity distribution of subterranean waters. As far as the drainage conditions deteriorate with depth, the circulation of water slows down and the salinity concentration of water naturally increases with depth.

4. The duration of time of the contact of water with the geological formations in the subsurface reservoirs and the continuity of the movement of water are important factors influencing the chemical change of subterranean waters.

5. The mobility of the chemical elements in the crust of weathering, the degree of dispersion of material along with the phases of weathering, and the magnitude

of the transporting forces determine the salinity concentration and the formation of chloride brines in the earth's crust.

6. While the salts least soluble in the water are precipitated first and the most soluble salt last, at any given time and at any distance from the intake area the chemical compounds of higher solubility will be found in water in greater relative abundance. The sodium chloride (common salt) tends therefore to be in the solution state as long as the extremely high salinity concentration of water is achieved (normally up to 354,000 p.p.m. and even 425,900 p.p.m.) (Table 39), and the appropriate physical-chemical environment in the subsurface reservoir causes its precipitation.

This process usually takes place when the temperature is about 25–35°C, and it is considered as one of the "hypergenic" processes (Fersman, 1934).

At the same time the salt waters (brines) with the higher specific gravity than that of fresh water tend to occupy the lower portion of the water-bearing formations.

7. In the oilfield areas the maximum concentration of water often occurs at or near the oil-water contact.

8. The structural features of the area, the lithology, thickness, and permeability of the strata are of understandable significance in the circulation of subterranean waters in the crust of weathering and the occurrence of water of various salinity.

9. The occurrence of the salt deposits in the formations located in the zone of circulation of waters is a factor of great importance in their salinity concentration. The salt-bearing rocks can, however, yield water of low salinity when the active water-exchange takes place.

10. The marine sediments of normal salinity found in the "closed" structures usually yield water of higher salinity.

11. The formation of chloride brines which occur not only in the marine deposits, but also in the fresh-water sediments and even in metamorphic and igneous rocks, is treated as chiefly due to the *metamorphism* of meteoric water.

12. Summarizing the concept advanced, it can be stated that the salinity distribution of subterranean waters obeys a definite hydrological and geochemical law which can be formulated as the *cycle of metamorphism of natural waters in the crust of weathering.*

The fundamental phases of this cycle are shown in Fig. 18.

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# Notes on the geochemistry of antimony

Hiroshi Onishi and E. B. Sandell
School of Chemistry, University of Minnesota, Minneapolis

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ABSTRACT

The meteoritic abundance of antimony, based on chondrites, is about 0·1 p.p.m. The metal phase of chondrites contains ~0·5 p.p.m. Sb. Antimony shows no decided preference for silicic or subsilicic rocks. The amount in igneous rocks (and in the upper lithosphere) is estimated as 0·1–0·2 p.p.m. Shales are variable in antimony, ranging from ~0·1 p.p.m. to several parts per million; the average may be 1 to 2 p.p.m. Limestone and sandstone normally contain less antimony than shales. Bauxite and phosphate rock may contain as much antimony as the richest shales. Oceanic red clay (Pacific) contains ~1 p.p.m. Sb, globigerina ooze a few tenths of a part per million. A rough estimate of the weight ratio Sb/As in the upper lithosphere is 0·1, not significantly different, when the experimental error is considered, from the value 0·05 for meteorites. Because of the low concentrations of antimony in igneous rocks and meteorites and the inadequate sensitivity of the photometric method, the abundance values for these must be looked upon as tentative.

After a study of the occurrence of arsenic in igneous and sedimentary rocks (Onishi and Sandell, 1955), it was thought desirable to attempt the determination of antimony in some of the same samples. The level of antimony in igneous rocks was found to be but little higher than the limit of the analytical method, so that work on these was restricted to composites, which have furnished a rough average. Sedimentary rocks as a whole contain more antimony than igneous rocks, and are more amenable to examination by the present method. Some individual values as well as averages have been obtained for these rocks. Approximate averages have also been obtained for chondrites as a whole, and for their metal phase.

## 1. Previous Data

The more pertinent abundance data for antimony are summarized in Table 1. The early averages of Clarke and Washington (1924) and of Berg (1925) for antimony in igneous rocks have been omitted as not being based on actual determinations. The Goldschmidt (1937) average of 1 p.p.m. Sb for igneous rocks is based on the assumption that the ratio As/Sb in these is the same as in arsenic- and antimony-rich sediments (iron ores and bauxites), namely 5, and that the arsenic content of igneous rocks is 5 p.p.m. The average of Preuss (1940) for the German granites is very approximate, because it coincides with the limit given by him for his spectrographic method involving fractional distillation of 3-g samples. The results of the Noddacks (1931) were obtained by an unspecified method.

## 2. Analytical Method

The procedure for antimony in silicate rocks has been described in detail (Onishi and Sandell, 1954). It consists in decomposition of the sample with sulphuric-hydrofluoric acids, precipitation of antimony as $Sb_2S_3$ by hydrogen sulphide from sulphuric-tartaric acid medium in the presence of copper as a collector, removal of gallium by ether extraction of the chloride, and final photometric determination of antimony with rhodamine B. Samples of 1 g. were usually taken, and transmission measurements were made with a Leitz-Rouy photometer (550 m$\mu$ filter) in a 1-cm cell. For less than 1 p.p.m. Sb the absolute error is not likely to exceed $\pm$0·2 p.p.m. For 1 to 2 p.p.m. Sb the error should lie within 20 per cent. Other elements, major or minor, in the amounts found in igneous and sedimentary rocks do not interfere.

*Table* 1. *Summary of literature data on abundance of antimony*

| *Material* | Sb (*p.p.m.*) | *Author* |
|---|---|---|
| *Igneous rocks* | | |
| Basalt, Kaiserstuhl; lava, Vesuvius | 5, 10 | Noddacks (1931) |
| Granite, Rhode Island; diabase, Va., U.S.A. | 0·6; 1·2* | Ward and Lakin (1954) |
| Composite of 14 German granites | ~0·3 | Preuss (1940) |
| Igneous rocks, average (estimated) | 1 | Goldschmidt (1937) |
| Igneous rocks, average | 0·4 | Noddacks (1934) |
| *Sedimentary* | | |
| Composite of 36 German shales | 3 | Preuss (1940) |
| Composite of 23 German sandstones | 1 | Preuss (1940) |
| Mansfeld copper-shale, average | 300 | Cissarz and Moritz (1933) |
| *Sulphides* | | |
| Pyrite, Norway, 2 samples | 10, 2 | Noddacks (1931) |
| Magmatic sulphides, average | 1 | Noddacks (1931) |
| *Meteorites* | | |
| Silicate phase of 42 stony meteorites | 0·1 | Noddacks (1930) |
| Troilite of 5 irons | 7·8 | Noddacks (1930) |
| Irons (16) | 2·0 | Noddacks (1930) |
| Chondrites, average | 0·64 | Noddacks (1934) |
| Troilite of Canyon Diablo iron | 4 | Noddacks (1931) |
| Mukerop iron | 5 | Noddacks (1931) |
| *Miscellaneous* | | |
| Ash of coal, Va., U.S.A. | 40 | Headlee and Hunter (1953) |
| Ash of German coal, maximum | 3000 | Otte (1953) |
| Hot spring water, Steamboat Springs, Nev. | ~0·1–0·4 | Brannock *et al.* (1948); White and Brannock (1950) |
| Sea-water | <0·0005 | Noddacks (1939) |
| Marine animals | 0·08–0·24 | Noddacks (1939) |

* By a field method for antimony.

Limestone (2 g) was treated with 4 *M* hydrochloric acid at room temperature, and the residue was filtered off and fused with sodium peroxide in a nickel crucible. The melt was taken up in hydrochloric acid and sulphide precipitation was then carried out in the combined filtrates. Phosphate rock (1 g) was dissolved in concentrated hydrochloric acid at room temperature. If an appreciable amount of residue remained, it was filtered off and fused with sodium peroxide.

Iron meteorites (0·5 g) were dissolved in aqua regia, and the solution was evaporated to a paste. Sulphuric acid (1 : 1) was added to the residue, and the solution was evaporated to strong fumes. This step was repeated. The residue was taken up in sulphuric acid, and reduction of ferric iron with hydroxylamine hydrochloride was carried out just before sulphide precipitation. As a precautionary measure, gold was separated by sulphurous acid reduction, with tellurium as a collector. Tests with steels showed satisfactory recovery of antimony.

For the determination of total antimony in chondrites, the sample (1 g) was first treated with aqua regia and evaporated almost to dryness. Sulphuric acid (1 : 2) was added to the residue, followed by evaporation to strong fuming. The residue was transferred to a platinum dish and decomposed with sulphuric-hydrofluoric acids.

Metal was separated from chondrites magnetically. Silica was determined in the separated metal and a correction for the weight of silicate was applied.

## 3. Discussion

Tables 2–5 list the antimony contents of the samples analyzed, together with the arsenic contents where available from earlier work. A summary of weighted averages is given in Table 6.

Because of the insufficient sensitivity of the analytical method, the averages for igneous rocks are only approximate. Two of the basalt and diabase composites contain what appears to be abnormally high amounts (0·9 and 1·3 p.p.m.) of antimony, five or ten times the amount in the other composites. Their omission in the computation of a basaltic average is probably justified. Antimony shows no marked preference for silicic or subsilicic rocks, and thus resembles arsenic. The values in Table 2 seem to indicate somewhat more antimony in silicic rocks, but the accuracy of the results does not warrant a positive conclusion.* The present granitic average of ~0.2 p.p.m. Sb is in agreement with Preuss's value of about 0·3 p.p.m. for a composite of fourteen German granites, but the approximate character of both figures must be emphasized. The weight ratio Sb/As in igneous rocks appears to lie in the range ~0·05–0·2. A tentative average for the antimony content of the lithosphere is 0·1–0·2 p.p.m. Goldschmidt's estimate of 1 p.p.m. antimony for the crustal rocks is certainly too high, perhaps by a factor of 5 or 10.

Shales are strongly variable in antimony. Some contain no more than igneous rocks, whereas others contain as much as a few parts per million. Too few shales have been examined in the present work to enable a satisfactory average to be established. The average of fourteen individually analyzed samples (one a small composite of 3) is 0·5 p.p.m. Sb, but the average of two composites representing seven American, thirty-six German and twenty-four Japanese shales is 2·4 p.p.m. The best that can be done is to take the average as 1–2 p.p.m. on the basis of the values in Table 3. The antimony content of shales as a whole may be as much as ten times greater than that of igneous rocks. Probably further work will show that antimony, like many other metals, tends to be concentrated in shales rich in carbonaceous matter and sulphides. But there is also evidence that antimony can occur in appreciable amounts in shales and slates not characterized by these substances, as for example in those containing relatively much ferric iron. Its presence in these may conveniently but rather vaguely be ascribed to fixation by adsorption on finely divided hydrous oxides and clay minerals. Probably antimony in sediments is present predominantly in the trivalent state. Antimony and arsenic do not vary together in shales. The weight ratio Sb/As in the samples examined varies from 0·01 to about 0·2

Since little antimony may be expected to enter quartz, calcite, or dolomite, sandstones and limestones should be low in antimony, and what is found should

* Bismuth apparently prefers silicic rocks. Preuss (1940), who alone has reported values for bismuth in rocks, found the surprising amount of 2 p.p.m. Bi in a composite of fourteen German granites; apparently bismuth was not detected in a composite of eleven German gabbros. If the granitic figure is representative, a marked concentration of bismuth in silicic rocks is indicated.

*Table 2. Antimony and arsenic in composites of igneous rocks*

| *No.* | *Composite* | Sb (*p.p.m.*) | As (*p.p.m.*) | Sb/As |
|---|---|---|---|---|
| 1 | Granite, U.S.A. (Calif., N.Y., etc.) and Canada (37)[1] | 0·2, 0·4 | 1·4 | 0·2 |
| 2 | Granite, U.S.A. and elsewhere (18)<br>Antarctica 3, Canada 4, Newfoundland 1, Rhodesia 1, New Hampshire 1, Rhode Island 1, New York 2, Missouri 2, central Texas 1, California 1, unknown locality 1. | 0·2, 0·2 | | |
| 3 | Granitic, Minnesota (11)<br>Granite porphyry (2), Benton Co. and Sauk Rapids; granite (2), Benton Co.; hornblende granite, Stearns Co.; quartz monzonite (2), Kanabec Co. and near Pierz, Morrison Co.; granodiorite (2), Benton Co.; granite-gneiss (2), Aitkin Co. and Morton | 0·1, 0·1 | 1·2 | ~0·1 |
| 4 | Granite, Llano region Texas (5) | 0·0, 0·1 | 0·9 | ~0·1 |
| 5 | Granitic, Japan and China (12)<br>Fukushima Prefecture 2, Gifu Pref. 3, Gumma Pref. 1, Ibaraki Pref. 1, Nagano Pref. 1, Okayama Pref. 1, Yamanashi Pref. 1, Prefecture unknown 1; China 1. | 0·1, 0·2 | 2·3[2] | ~0·1 |
| 6 | Granite-gneiss (14)<br>Canada, U.S.A. and elsewhere | 0·3, 0·4, 0·3 | 1·1 | 0·3 |
| 7 | Silicic, U.S.A. (7)<br>Rhyolite, White Pine, Nev.; quartz keratophyre, Marblehead, Mass.; quartz monzonite, Boulder Co., Colo.; muscovite-biotite granite (2), Concord, N.H. and Mt. Airy, N.C.; hornblende granite, Rockport, Mass.; alkalic granite, Quincy, Mass. | 0·6, 0·6 | 1·4 | 0·4 |
| 8 | Diorite and quartz diorite, western Canada (10) | 0·1, 0·3 | | |
| 9 | Andesite, Japan (6)<br>Gifu Prefecture 1, Kumamoto Pref. 1, Nagano Pref. 4. | 0·2, 0·2 | 1·9 | 0·1 |
| 10 | Basalt and diabase, mostly N.A. (11)<br>Basalts: Alaska 1, Newfoundland 1, Connecticut 2, Idaho 1, India 1; diabases: New York 1, Virginia 2, Antarctica 2. | 0·3, 0·3 | | |

*Table 2—continued*

| *No.* | *Composite* | Sb (*p.p.m.*) | As (*p.p.m.*) | Sb/As |
|---|---|---|---|---|
| 11 | Basalt and diabase, mostly U.S. (6) New Jersey 2, Colo. 2, Wash. 1, Sicily 1 | 0·9, 0·8, 1·0 | 2·6 | 0·4 |
| 12 | Basalt and diabase, Minn. and Wis. (5) Keweenawan | 0·1, 0·1 | 1·0 | ~0·1 |
| 13 | Basalt, Mich. (12) Greenstone flow | 0·1, 0·1 | 0·8 | ~0·1 |
| 14 | Basalt, Mich. (8) Kearsarge flow | 0·1, 0·1 | 1·6 | <0·1 |
| 15 | Olivine basalt, Oregon (7) | 0·1, 0·1 | 0·8 | ~0·1 |
| 16 | Basalt and diabase, Japan (5) Gifu Prefecture 1, Gumma Pref. 1, Niigata Pref. 1, Oshima Volcano 1, not known 1. | 1·3, 1·4 | 2·0 | 0·7 |
| 17 | Gabbro, U.S.A. and Canada (4) Mass. 1, N.C. 1, Colo. 1, Ontario (Sudbury) 1. | 0·1, 0·2 | 2·1 | ~0·1 |
| 18 | Gabbro, Duluth, Minn. (5) | 0·1, 0·1 | 0·9 | 0·1 |
| 19 | Ultramafic, U.S.A. and Canada (13) Peridotite 4, dunite 3, bronzitite 1, harzburgite 2, pyroxenite 1, unspecified ultramafic 2. | 0·1, 0·1 | | |
| 20 | Ultramafic, U.S.A. (4) Serpentine, N.J. 1, Calif. 1; dunite, N.C. 1; lherzolite, Md., 1. | 0·0, 0·2 | 0·9 | ~0·1 |

[1] Figures in parentheses indicate number of samples, equal weights of each.
[2] Average of 10.

be present largely in the shaly or other foreign component. At least some bauxites are relatively high in antimony. The two samples examined contained approximately 2 p.p.m. One of these, in which arsenic had also been determined, showed a high Sb/As ratio of 0·4. Phosphate rock is evidently variable in antimony; a sample of Tennessee brown contained 0·2 p.p.m., one of Florida pebble phosphate 1·2 p.p.m. (the latter has Sb/As = ~0·6). From phosphate rock, antimony appears to find its way into manufactured phosphoric acid. Reagent grade 85 per cent phosphoric acid was found to contain 1 p.p.m. Sb.

Oceanic red clays are clearly enriched in antimony compared to igneous rocks. An average of 1 p.p.m. Sb is indicated, roughly one-tenth of the arsenic content. Globigerina ooze is very low in antimony, a composite of six Pacific samples showing 0·1–0·2 p.p.m. These values are comparable to those of the somewhat analogous shales and carbonate rocks.

*Table 3. Antimony and arsenic in sedimentary rocks and slates*

| | Sb (*p.p.m.*) | As (*p.p.m.*) | Sb/As |
|---|---|---|---|
| *Shales* | | | |
| Composite (3), St. Croix Falls, Wis. | 0·1, 0·1 | 6·0 | ~0·02 |
| Pyritic shale, St. Croix Falls, Wis. | 0·3,[1] 0·3[1] | 16·2 | ~0·02 |
| Composite of Decorah shale (4), Minn. | 0·1, 0·3, 0·1 | 6·9 | ~0·02 |
| Shale, arenaceous, Green Co., N.Y. | 0·3, 0·4 | 24·4 | ~0·02 |
| Shale, calcareous, Livingston, Co., N.Y. | 0·5, 0·5 | 6·8 | 0.07 |
| Shale, carbonaceous, Green Co., Pa | 0·3, 0·2 | 6·0 | 0·05 |
| Shale, bituminous, Le Roy, N.Y. | 2·2, 2·5 | 59 | 0·04 |
| Shale, green, Rochester, N.Y. | 0·4, 0·7, 0·5 | 22·4 | ~0·02 |
| Oil shale (tasmanite), near Latrobe, Tasmania | 0·2,[1] 0·2[1] | 6·5 | 0·03 |
| Composite of shales (7), Alaska and U.S.A.[2] | 2·5, 2·6 | 12·3 | 0·21 |
| Shale, Itsukaichi, Tokyo, Japan | 0·3, 0·4 | 12·7 | 0·03 |
| Shale, Kamitakara, Gifu Pref., Japan | 1·0, 0·7 | 9·3 | 0·1 |
| Shale, Yokote, Akita Pref., Japan | 0·2, 0·2 | 2·6 | 0·08 |
| Shale, unspecified locality, Japan | 0·2, 0·3 | | |
| Shale, Kawai, Gifu Pref., Japan | 0·2, 0·2 | 30·5 | ~0·01 |
| Composite of preceding 3 shales | 0·4[1] | | |
| Non-weighted composite of Japanese (24) and European shales[3] (36) | 2·3[1] | 10·2 | 0·23 |
| *Slates* | | | |
| Slate, red, Granville, N.Y. | 1·4, 1·7, 1·9 | 3·3 | 0·5 |
| Slate, green, Powlet, Vt. | 0·5, 0·5 | 4·3 | 0·12 |
| Slate, red, Cuyuna Range, Minn. | 0·3, 0·5 | 11·6 | 0·03 |
| *Limestone and sandstone* | | | |
| Composite of limestones[4] (9) | 0·2, 0·3 | 2·3 | 0·1 |
| St. Peter sandstone, Minneapolis, washed with HCl | 0·0, 0·0 | 1·0 | <0·1 |
| *Miscellaneous* | | | |
| Bauxite, Demerara, British Guiana | 1·7, 2·0 | 4·5 | 0·4 |
| Bauxite, Haiti, composite of main Acetillar ore body | 2·1, 2·5 | | |
| Pebble phosphate, Brewster, Fla. | 1·2, 1·3 | 2·3 | 0·56 |
| Phosphate rock, Tennessee Brown, Natl. Bur. Standards sample 56a | 0·2, 0·2 | | |

[1] Residue from hydrofluoric-sulphuric acid decomposition fused with sodium peroxide.

[2] 3 calcareous shales and 1 organic shale, Alaska; Cason shale, Ark.; shale, N. Dak.; shale, red, Maine.

[3] Because of insufficient material the European (Noll, 1934) and Japanese (Minami, 1935) composites were mixed in equal amounts. Preuss (1940) found 3 p.p.m. Sb in the European composite.

[4] Argillaceous limestone, Trenton Falls, N.Y.; chalk, Dover, England; 2 dolomitic limestones, Rochester, N.Y. and Knoxville, Tenn.; limestones, gray, Onondaga Co., N.Y. and Ruth, Nev.; 2 limestones, Concrete, Colo. and Mt. Lebanon, Syria; limestone, oolitic, Bedford, Ind.

Chiefly because the average amount of antimony in sedimentary rocks is not well established, no satisfactory comparison of the escaping tendencies of antimony and arsenic can be made. From the available data it appears that they are not greatly different. Antimony is present, with arsenic, in the waters of hot springs regarded as connected with magmatic activity. In waters of

*Table 4. Antimony in deep-sea deposits*

| | Location | | Depth (*m*) | Sb (*p.p.m.*) |
|---|---|---|---|---|
| Composite of red clays, Pacific Ocean | 30° 28·0′N | 135° 47·0′E | 4363 | 1·3, 1·4 |
| | 15° 10·0′ | 154° 34·5′ | 5219 | |
| | 31° 33·5′ | 136° 20·5′ | 4096 | |
| | 13° 39·5′ | 158° 49·0′ | 5794 | |
| Composite of red clays, Pacific Ocean | 5° 13·0′N | 140° 40·0′E | 4884 | 0·6, 0·7 |
| | 9° 25·5′ | 126° 40·5′ | 5844 | |
| | 6° 47·0′ | 139° 27·0′ | 4293 | |
| | 6° 43·0′ | 141° 27·5′ | 4743 | |
| Composite of globigerina ooze, Pacific Ocean | 16° 6·5′N | 143° 16·5′E | 2140 | 0·1, 0·2 |
| | 8° 0·0′ | 151° 44·0′ | 3729 | |
| | 3° 17·5′ | 159° 32·5′ | 3860 | |
| | 3° 19·0′ | 160° 39·0′ | 3659 | |
| | 6° 34·0′ | 144° 41·5′ | 3874 | |
| | 5° 32·0′ | 145° 27·0′ | 4540 | |

Steamboat Springs, Nevada, the weight ratio Sb/As has been found to have the values 0·10, 0·18, 0·28, and 0·37, the average of the four samples being 0·15 (Brannock *et al.*, 1948; White and Brannock, 1950). This is similar to the average ratio in shales. In a thermal spring water of Umnack Island, a higher ratio of 0·42 was found, but this is counterbalanced by other waters of the same

*Table 5. Antimony and arsenic in meteorites*

| | Sb (*p.p.m.*) | As (*p.p.m.*) | Sb/As |
|---|---|---|---|
| Iron meteorite, Canyon Diablo, Ariz. | 0·7, 0·8, 0·9 | 8·1 | 0·1 |
| Iron meteorite, Henbury, Australia | 0·4, 0·5, 0·7 | 3·6 | 0·14 |
| Composite I of chondrites (7)[1] | 0·1, 0·1 | 2·2 | ~0·05 |
| Metal phase of composite I | 0·4 | 11 | 0·04 |
| Composite II of chondrites (7)[2] | 0·1, 0·1 | 2·2 | ~0·05 |
| Metal phase of composite I and II | 0·5, 0·7 | 12 | ~0·05 |

[1] Arriba, Colo.; Beenham, N. Mex.; Cope, Colo.; Cotesfield, Neb.; Morland, N. Mex.; Plainview, Texas; Roy, N. Mex.

[2] Alamogordo, N. Mex.; Estacado, Texas; Gladstone, N. Mex.; Kingfisher, Okla.; Gruver, Texas; Ladder Creek, Kans.; Melrose, N. Mex.

locality in which no antimony was found, although the arsenic content ranged up to 3·8 p.p.m. (Byers and Brannock, 1949). In such hot spring waters, antimony is doubtless present principally as thioantimonite. At some locations, as at Steamboat Springs, stibnite is being deposited.

*Meteorites.* Although the present meteoritic data are neither extensive nor

highly accurate, they probably are closer to the truth than earlier values. The Noddack (1934) abundance figures (Table 1) are very likely too high. The metal phase of the chondrites examined contains about 0·5 p.p.m. Sb (±50 per cent), and the chondrites as a whole roughly 0·1 p.p.m. The metal content of the chondrite composites is 12 per cent. The metal phase then accounts for roughly 0·05 to 0·1 ($0·5 \times 0·12 = 0·06 \pm \sim 0·03$) p.p.m. Sb of the total content of ~0·1 p.p.m. This leaves but little antimony to be contributed by the silicate and troilite if the total content is actually 0·1 p.p.m. But this content might well be 0·2 p.p.m. because of the large experimental error in the determination, so that

*Table* 6. *Summary of averages*

| | Sb (*p.p.m.*) | Sb/As |
|---|---|---|
| Granitic rocks (97)[1] | 0·24 | 0·2[2] |
| Intermediate rocks (16) (diorite, quartz diorite, and andesite) | 0·2 | ~0·05[3] |
| Basalts and diabases (49,[4] 43[5]) | 0·24,[4] 0·15[5] | ~0·1 |
| Gabbros (9) | 0·1 | 0·05-0·1 |
| Ultramacfic rocks (17) | 0·1 | 0·1 |
| Shales | 1-2 | ~0·1 |
| Oceanic red clays (8) | 1 | ~0·1 |
| Chondrites (14) | 0·1 | ~0·05 |
| Metal phase of chondrites (14) | 0·5 | 0·05 |

[1] Composite No. 7 (silicic) not included. If included average is 0·26.
[2] Based on 79 samples.
[3] Based on 8 samples.
[4] Japanese composite No. 16 omitted. If included, average is 0·35.
[5] Composites Nos. 11 and 16 omitted.

no reliable value can be assigned to the non-metallic portion of the chondrites. Doubtless there is much more antimony in the troilite than in the silicate, but its amount in the former must also be left undecided.

In Fig. 1 the meteoritic abundances (or approximate cosmic abundances) of arsenic, antimony, and their neighbours of odd atomic number are plotted. The abundances of copper and gallium refer to chondrites, and are based on unpublished analyses of composites (copper by Jean'ne Shreeve, gallium by H. Onishi). Other values are based on the ratio 10 silicate phase : 2 metal : 1 troilite accepted by Goldschmidt as representing the average of meteorites, but values based on chondrites alone probably would not differ to any important extent. The bromine (Behne, 1953) and iodine values are very uncertain. Arsenic and antimony occupy minima in the sequence of adjacent elements of odd atomic number. The minimum for arsenic may be regarded as established; that for antimony may or may not be real. At any rate, antimony is one of the least abundant elements. Other metals that are, or may be, less abundant than antimony include cesium, bismuth, thallium, and mercury. Bismuth is doubtless actually less abundant than antimony, but probably not much less.

*Acknowledgements*—We are indebted to Dr. S. S. Goldich for placing numerous igneous rock samples at our disposal, to Mr. R. A. Burwash for some Canadian intermediate rocks, to Drs. R. E. Stevens and M. K. Carron for a number of American shales, to Drs. E. Minami and K. Sugawara for European and Japanese shale composites, and to Dr. H. Hamaguchi for deep-sea sediments.

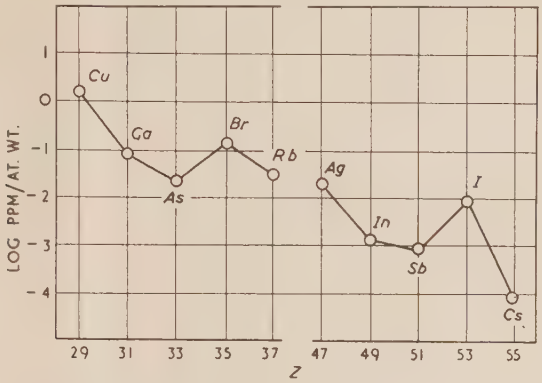


Fig. 1. Log of the atomic abundance, expressed as parts per million/atomic weight, of elements 29–37 and 47–55 in meteorites.

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# Book reviews

**Gmelins Handbuch der anorganischen Chemie,** 8. Auflage. System-Nummer 13: Bor, *Ergänzungsband*, VII, 253 S. mit 28 Fig. Preis: Kart. DM 140. System-Nummer 62: Gold, Lieferung 2—V, 306 S. mit 20 Fig. Preis: Kart. DM 168. Herausg. Gmelin-Institut, Clausthal-Zellerfeld. Verlag Chemie, Weinheim/Bergstr. 1954.

Im Egänzungsband zu dem 1926 erschienenen Band Bor ist die Literatur bis Ende 1949 nachgetragen, insbesondere ist ein neues Kapitel über die Geochemie des Bors aufgenommen worden. Das Vorkommen des Bors hatte im Hauptband nur etwa 8 Seiten beansprucht, hier sind es 45 Seiten, an die sich noch 6 Seiten topographische Übersicht und 6 Seiten über die Borminerale anschliessen. Die übrigen 197 Seiten bringen das Element Bor und seine Verbindungen.

In der Lieferung über das Gold wird die Geochemie auf 32 Seiten behandelt, die topographische Übersicht umfasst hier 144 Seiten, die Minerale sind nur ganz kurz auf 1/1/2 Seiten angeführt. Die übrigen 127 Seiten der Lieferung sind dem Element Gold gewidmet.

Beide geochemischen Abschnitte bringen eine grosse Fülle von Literaturangaben in der bereits in früheren Besprechungen erwähnten Gliederung. Stärker als bei anderen Bänden ist dem Referenten besonders bei dem Band Bor aufgefallen, dass eine solche vollständige Literaturzusammenstellung für den Benutzer auch Nachteile hat, weil nicht zwischen wichtigeren und unwichtigeren Arbeiten unterschieden ist und die gegensätzlichen Meinungen der Autoren nebeneinander aufgeführt werden. Das liegt aber wohl in der Natur eines solchen Handbuchs. Trotz der dadurch manchmal verursachten Mehrarbeit wird jeder, der sich mit der Geochemie dieser Elemente befasst, die Literaturzusammenstellung mit grossem Vorteil benutzen.

C. W. Correns

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L. H. Ahrens: **Quantitative Spectrochemical Analysis of Silicates.** 122 pp. 1954. Pergamon Press, London. 25s.

This small book does not attempt to cover the entire field suggested by its title, but rather describes certain of the direct-current arc techniques worked out in the Cabot Spectrographic Laboratory of the Massachusetts Institute of Technology, and discusses one or two related topics which were not fully dealt with in the author's earlier book (*Spectrochemical Analysis*, Addison-Wesley, 1950). Separate chapters consider the alkali metals, the volatile metallic group, the involatile elements, fluorine, and the common elements other than sodium and potassium. The approach is to discuss the advantages and disadvantages of different arc excitation techniques for specific problems, rather than to present a comprehensive method of general application.

Chapters on analytical results obtained in collaboration with other laboratories for two rock standards, a granite and a diabase, and on the lognormal distribution of spectrochemical error, are of interest to geochemists and others concerned with the interpretation of analytical results as well as to practising spectrochemists.

A few minor misprints have been noted. For instance, the page reference in the first line of p. 17 should read 59–61, and Messrs. Champion's address (p. 18) is Wardour Street. One or two references cite "in press" without indicating the journal, thereby causing unnecessary search by the interested reader.

Throughout the text are to be found points of considerable practical interest to those carrying out the arc emission analysis of all types of material, and the book is undoubtedly one which should be on the shelves of all who are so engaged.

R. L. Mitchell

## ANNOUNCEMENT

# Reference samples of isotopic abundance*

At the request of the U.S. Geological Survey, the National Bureau of Standards has undertaken a programme for the preparation and distribution of reference samples of isotopic abundance in forms suitable for mass spectrometric analysis. The National Bureau of Standards will serve as a clearing house for data on the isotopic abundance ratios as measured by co-operating laboratories and will distribute the accumulated data with each sample requested.

Laboratories throughout the world are engaged in mass spectrometer research on variations in natural isotopic abundance, using a variety of techniques. Different laboratories are equipped to measure mass spectra of gases, of compounds evaporated from a furnace, and of ions emitted

*Table* 1. *Reference samples of isotopic abundance*

| *Element* | *Compound* | *Source* |
|---|---|---|
| H | $H_2O$ | Steam condensate from Potomac River water |
| | $H_2$ | From $H_2O$ |
| D | $D_2O$ | Commercial-99·8 atom per cent D |
| | $D_2$ | From $D_2O$ |
| He | | Atmosphere (commercial) |
| Ne | | Atmosphere (commercial) |
| A | | Atmosphere (commercial) |
| Kr | | Atmosphere (commercial) |
| Xe | | Atmosphere (commercial) |
| Li | Spodumene | King's Mountain, N.C. |
| | $Li_2CO_3$ | Commercial |
| K | $K_2CO_3$ | Commercial |
| Rb | $Rb_2CO_3$ | Commercial |
| Sr | $SrCO_3$ | Commercial |
| Mg | $Mg(OH)_2$ | Commercial |
| Cl | NaCl | Marine (commercial) |
| Br | NaBr | Marine (commercial) |
| S | Native sulphur | Wharton County, Texas |
| | $SO_2$† | Sulphur and air |
| O | $O_2$† | Air |
| N | $N_2$† | From air |
| Pb | Galena | Ivigtut, Greenland |
| | $PbI_2$ | From galena |
| | $Pb(CH_3)_4$† | From galena |
| Ag | $AgNO_3$ | Commercial |
| Cd | $CdI_2$ | Commercial |
| Hg‡ | Element | National Physical Laboratory |
| B | $BF_3$ | Commercial |
| Si | $SiF_4$ | Commercial |
| Ca,C,O | Limestone | Solenhofen, Bavaria |

* This programme has been initiated with the support of the U.S. Atomic Energy Commission.
† These will be available in the near future.
‡ This is a small sample which was carefully measured by several mass spectrometer laboratories.

by a hot filament. Different compounds of the element are required for these different techniques. Table 1 lists reference samples that are now available for distribution or will soon be available. The gaseous samples are equivalent to about 3 ml at 1 atmosphere sealed in break-seal containers. Solid samples are about 0·1 g sealed *in vacuo* in pyrex tubes. Liquids are in break-seal tubes.

There is an immediate need to accumulate data on these samples, and laboratories wishing to receive samples and measure them should write to the address below. These laboratories will be kept informed concerning data obtained by others.

The programme will continue with preparation of other compounds useful as reference samples and with research on compounds best adapted to isotope abundance measurements.

Fred. L. Mohler
*Chief Mass Spectrometry Section,*
*National Bureau of Standards,*
*Washington, D.C.*

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AHRENS, L. H. (1952) *Geochim. et Cosmochim. Acta* **2**, 168.

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